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 ≠ 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···HX– will lead to a heterodimer. Likewise, two different carboxylic acids substituted with Y and HX

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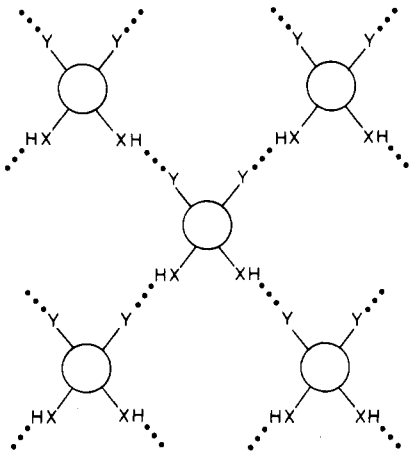
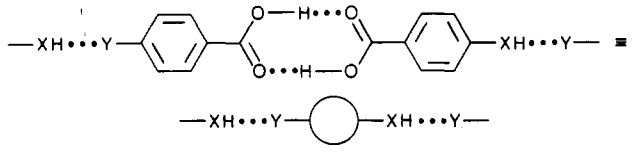


3

respectively could hydrogen bond together as an acentric carboxylic acid dimer,[6] shown below. The acid dimers could then associate into acentric chains through Y···HX bonds,[7] corresponding to **2**.



Compound I was designed to correspond to **3**. The nitro, Y, and amino, XH, groups were chosen because hydrogen-bond interactions between these groups are weaker than the carboxylic acid interactions so they should not interfere with acid dimerization.

Cocrystals of I were prepared by evaporation of a methanol solution of equimolar amounts of 4-ABA and 3,5-DNBA. The crystals grew as large orange trapezoids, with the (100) face prominent[8] (Figure 1). The solution ^{1}H NMR spectrum of a single crystal confirmed that both reagents were present in stoichiometric amounts. The solid-state infrared spectrum of a powder prepared from one single crystal of the complex showed distinct differences from spectra of either starting reagents. In particular, the -NH stretching bands were shifted to higher frequency in the complex as compared to 4-ABA (3495 and 3394 cm^{-1}, vs 3461 and 3364 cm^{-1}). The melting point of compound I is 204.5–206.0 °C compared to 188.0–189.0 °C for 4-ABA and 203.0–205.0 °C for 3,5-DNBA. Second harmonic generation measurements confirmed that the crystal is acentric.[9] The crystal structure was solved to confirm the assignment of the hydrogen-bond pattern.[10] An ORTEP drawing of the hydrogen-bonded motif is shown in Figure 2.

The complex packs on a crystallographic C_2 axis such that the molecular dipole is parallel to the 2-fold crystal axis. Such a relationship between a molecular dipole and the 2-fold axis has been shown to result in loss of phase matchability,[2] consistent with our nonlinear optical measurements. The nitro groups form weak three-center hydrogen bonds (O···HN = 2.43 (1), 2.58 (1) Å) to the aniline hydrogens on neighboring glide related molecules ($\bar{x}+^3/_4$, $y+^1/_4$, $z+^3/_4$). The three-center bond corresponds to the typical hydrogen-bond pattern found previously for nitroaniline compounds.[4c] The acid dimers have disordered protons consistent with the 2-fold symmetry requirements. The (100) layers, which are polar as well as acentric,[11] are buckled and pack one on top of another by translation symmetry so the polarity of the two-dimensional hydrogen-bonded network is transferred to the entire three-dimensional structure.[12]

Compound I can also be prepared by a solid-state method involving simply grinding the two pure reagents together.[13] Complexation begins immediately as evidenced by a color change from off-white to bright yellow and by changes observed in the -NH infrared stretching bands of the solid mixture. Complete conversion to the product occurs after grinding the sample in a Wig-L-Bug for at least 5 min. The product obtained by this method gives the same X-ray powder pattern as crystals of I obtained from solution cocrystallization.

A series of related cocrystal complexes has been prepared where carboxylic acids are used as the primary hydrogen-bond contact between two different molecules.[14] Cocrystalline complexes have also been made with other primary linking groups such as pyridine *N*-oxides with alcohols or amines. Further work on characterizing these structures is in progress. The advantage of cocrystal design over homogeneous crystal design is that many different molecular components bearing the requisite proton donors and acceptors can be cocrystallized together into solid-state

(6) (a) Leiserowitz, L. *Acta Crystallogr.* **1976**, *B32*, 775–802. References to cocrystals of acids which show this typical dimer pattern include: (b) Cocrystals of cinnamic acids: Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1905–1912. (c) Crystal structures of complexes between amides and carboxylic acids: Huang, C.; Leiserowitz, L.; Schmidt, G. M. J. *J. Chem. Soc., Perkin Trans. 2* **1973**, 503–508. (d) Cocrystals of carboxylic acids with nucleotide bases: Tamura, C.; Sakurai, N.; Sato, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1473–1479. In some instances, an acid–base pair cannot form cyclic dimers; nevertheless, hydrogen-bonded cocrystals can still be grown. For example: (e) 4-aminobenzoic acid with 4-nitropyridine *N*-oxide: Lechat, J. R.; Main, P.; Santos, R. H. deA. *Acta Crystallogr.* **1984**, *A40*, C264, and private communication; (f) Salicyclic acid···nicotine: Kim, H. S.; Jeffrey, G. A. *Acta Crystallogr.* **1971**, *B27*, 1123–1131.

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(8) Miller indices of crystal faces, shown below, were determined by optical goniometry. The first set of Miller indices on each line represents one of the crystal faces of I, followed by the indices of intersecting faces (interfacial angles determined by goniometry given first, calculated angles (degrees) in brackets): (100); (111) = 72.8 [72.8], (10$\bar{1}$) = 46.2 [46.2], (1$\bar{1}$1) = 72.6 [72.8], ($\bar{1}$0$\bar{1}$) = 45.9 [46.1]; (111); (10$\bar{1}$) = 89.9 [89.0], (1$\bar{1}$1) = 50.8 [50.6], ($\bar{1}$0$\bar{1}$) = 64.6 [64.7]; (10$\bar{1}$); (1$\bar{1}$1) = 89.1 [89.0], ($\bar{1}$0$\bar{1}$) = 87.9 [87.7]; (1$\bar{1}$1); ($\bar{1}$0$\bar{1}$) = 64.6 [64.7].

(9) These measurements were done on a home-built Kurtz and Dougherty device for measuring second harmonic intensities from powders (Dougherty, J. P.; Kurtz, S. K. *J. Appl. Crystallogr.* **1976**, *9*, 145–158). The intensities observed were about as strong as those of a urea standard. The results were corroborated by independent measurements done at the IBM Laboratories in San Jose, CA, on powder samples and on a single crystal. Preliminary single-crystal measurements indicated that the material is not phase matchable.

(10) Crystal data for compound I: a = 21.49 (3), b = 4.041 (7), c = 20.65 (2) Å, $\alpha = \beta = \gamma = 90°$, *Fdd2*, Z = 8, D_x = 1.48 g/cm^3, Mo Kα, R_w = 0.032, R_f = 0.029 for 618 reflections, $I > 1\sigma(I)$; Enraf-Nonius diffractometer, direct methods, full-matrix least-squares refinement; all atoms were refined anisotropically except for hydrogens, which were set at idealized positions with fixed temperature factors. Complete crystal structure details will be reported elsewhere.

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(12) Compounds with meta-substituents, such as 3,5-dinitrobenzoic acid, are more likely than compounds with other substitution patterns to pack in acentric space groups (see ref 11 and: Desiraju, G. R.; Krishna, T. S. R. *Mol. Cryst. Liq. Cryst.* **1988**, *159*, 277–287). The acentricity observed in the two-dimensional hydrogen-bonded sheets of I, however, is controlled by the nature of the hydrogen bonds and not by the topology of the individual molecules.

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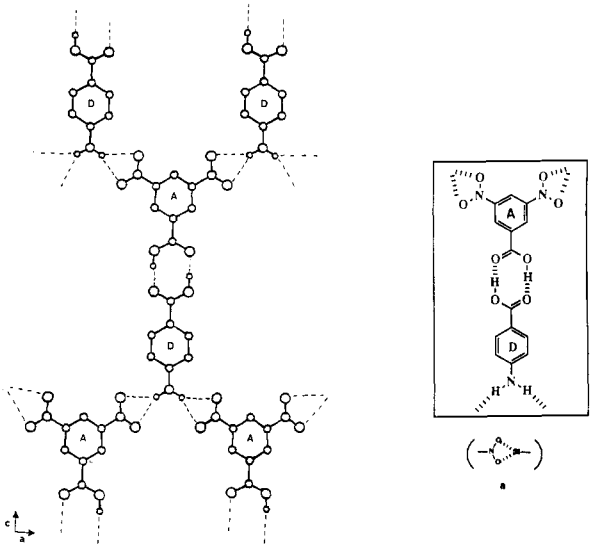
(14) The following cocrystals of benzoic acids have been made and chemically characterized in our laboratory: 4-aminobenzoic acid with 4-chloro-3,5-dinitrobenzoic acid, 4-nitrobenzoic acid, 3,4-dinitrobenzoic acid, and 3,5-dinitrobenzamide, respectively; 4-nitropyridine *N*-oxide with 4-chloro-3,5-dinitrobenzoic acid, 4-nitrobenzoic acid, and 3-hydroxybenzoic acid; and 4-aminobenzamide with 3,5-dinitrobenzoic acid.



I

Figure 2. ORTEP drawing of the hydrogen-bonded aggregate of I, viewed in projection onto the (010) crystal plane. The labels A and D refer to the molecules of 4-aminobenzoic acid and of 3,5-dinitrobenzoic acid, respectively. Hydrogen bonds are indicated by dashed lines. The polar nature of this aggregate is evident since all the nitro groups of A are pointing to the top of the figure and all the amino groups of D are pointing to the bottom. The array is not strictly planar since the interplanar angle between the mean plane of the NO_2 group and the hydrogen to which it is bonded (a) and the plane of the NH_2 group is 39°.

structures with predictable hydrogen-bond patterns. Such predictable patterns can be used to control various aspects of a crystal packing pattern, including the centric or acentric nature of the whole crystal or of subsets of the crystal. By choosing molecules that self-associate by hydrogen bonding into acentric aggregates, the resulting three-dimensional packing pattern is often biased to be acentric also,[15] so this method provides a useful alternative to chiral substitution[16] or inclusion in chiral clathrates[17] for preparing acentric nonlinear optical materials.

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Nonaqueous Perfluorocarbon-Derived Gold Colloids. Clustering of Metal Atoms in Fluorocarbon Media. 1

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Recently, we reported the successful preparation of colloidal gold[2] and palladium[3] in nonaqueous media by a process of atom clustering in excess organic solvent at low temperature. The metal atom vapor synthesis technique and apparatus have been described elsewhere.[4] By using polar organic solvents, this method yielded stable purple and black sols with gold and palladium, respectively. On the basis of this success, we have been studying the clustering of Au atoms in fluorocarbon media. Au/perfluorocarbon sols might be expected to possess unique properties imparted by the low chemical reactivity, polarity, and surface tension associated with perfluorocarbon solvents. Indeed, our initial findings show that very small gold particles can be prepared that exhibit quite unusual properties regarding aggregation. Initial studies of these unique materials are reported herein.

Au atoms have been codeposited with excess perfluorocarbon solvent vapor at 77 K. Perfluorotri-*n*-butylamine (PFTA) was most often used. The frozen matrix was light brown and yellow, became darker brown with warming, and was dark brown–black at room temperature. The resulting mixture was not a solution but rather a slurry in which the colored material settled. Nevertheless, it was found that the residue could be dispersed in polar organic solvents yielding brown, cola-colored solutions.

The recovery and dispersion of the particles could be accomplished in two ways. The PFTA, in which the particles are not "soluble", was removed by vacuum filtration, and the new solvent (acetone or ethanol, for example) introduced to dissolve the filter cake and form the brown solution. Alternatively, the Au particles were transferred from the slurry into the polar organic phase by solvent extraction, the PFTA being immiscible with most familiar solvents.

These PFTA-derived Au particles are quite selective with regard to dispersion in different solvents. For example, they could be dissolved in light aliphatic alcohols, ketones, aldehydes, and tetrahydrofuran (THF). They dissolved in, as well as reacted with, pyridine and its derivatives. The particles were insoluble in hydrocarbons, diethyl ether, and water. The ability to dissolve in most polar organics, but not in water, suggests a donor–acceptor interaction that requires the solvent to be a better Lewis base than water. This correlation between solvent functionality and the ability to dissolve the colloidal particles finds a parallel in the earlier work,[2] in which stable colloids were developed only when the codeposited solvent was a polar organic.

Transmission electron microscopy (TEM) studies[5] revealed that Au atoms had initially clustered to form roughly spherical particles ranging from 1 to 2 nm in diameter along with some larger aggregates; aging in solution for periods ranging from a few days to a few weeks led to further aggregation to form stable colloidal particles in the 2–10-nm range (Figure 1). Analysis of histogram data with a log probability graph yielded a straight line to indicate the distribution is log normal. The median size was found to be 3.4 nm with a geometric standard deviation of 1.5. Unlike the sols produced by the earlier method of direct Au/acetone codeposition in which the individual particles

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(5) TEM samples were prepared placing a drop of solution on a carbon-coated Cu grid; the solvent was allowed to evaporate.

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