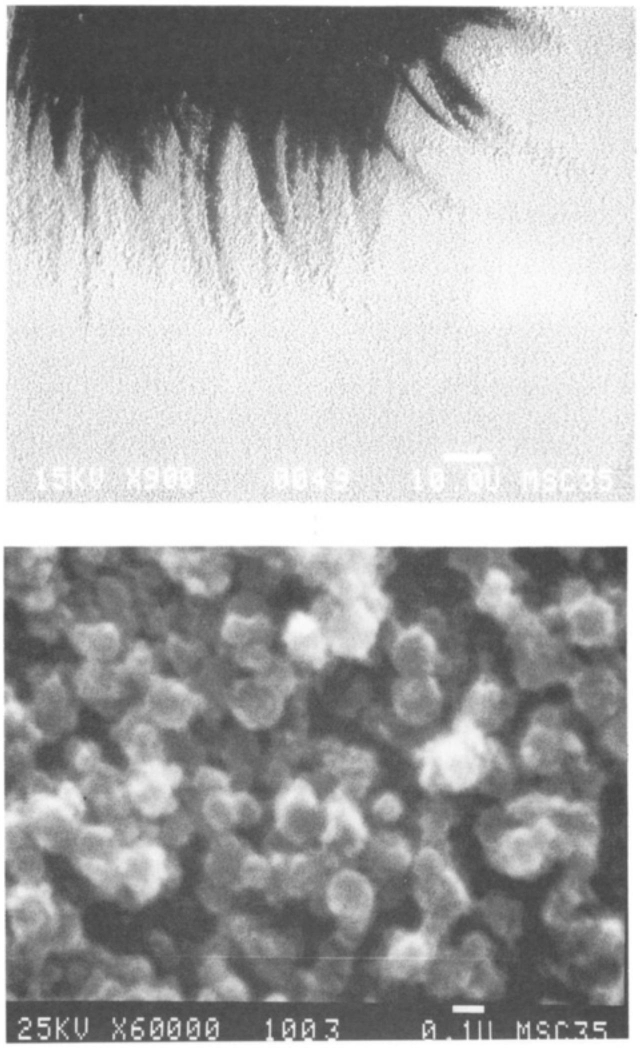

Figure 4. SEM images of TiO_2 particles made by electrospray deposition from a 1.0×10^{-2} M solution with ammonium acetate (1.0×10^{-3} M) over a period of 21 h. (top) Magnification of 900× with some particles removed by a brush (bar = 10 μm), (bottom) magnification of 60 000× (bar = 0.1 μm).

particles. Electron diffraction patterns (TEM) indicated that the particles were amorphous.

After several hours of electrospraying, some particles had accumulated on the inside wall of the glass tube. This suggested that the central electric field may have been weakened by the back-ionization[18] caused by particles on the collector; the charge on the collected particles may not have been dissipated very efficiently because the nanoparticles themselves were nonconductive. To provide some conductance, ammonium acetate was dissolved in the solution. When the salted solution was electrosprayed, no nanoparticles accumulated on the inside wall of the tube during many days of operation. Without added salt it was impossible to collect a large amount of material on any type of collector including glass, but with salt present, a much thicker layer accumulated on the collector (Figure 4, top). A portion of the deposit was easily removed from the glass substrate to show the thickness of the deposit. For these experiments, the concentration of the precursor solution was 1.0×10^{-2} M, from which a bimodal distribution was expected, but only larger particles were seen within the limits of resolution (Figure 4b). After they were heated at 700 °C for 12 h, thin-film XRD analysis of these particles showed that they contained only peaks at 25.3, 36.9, 37.8, 38.6, and 48.0° (2θ), consistent with the formation of anatase.[19] After calcination, the appearance and size of the particles were unchanged.

In summary, the conditions used to make nanoparticles from a gel-forming, metal–organic compound in an organic solvent by the electrospray method were the following: (1) a multijet spray formed very small droplets; (2) a very low concentration of precursor facilitated the process in (1); (3) sufficient path length allowed the particles to dry before they struck the collector; (4) to keep collection efficiency high, the aerosol was "focused" into a small area; (5) adding NH_4OAc to the solution increased the efficiency of collection.

The composition of the as-formed nanoparticles, the mechanism by which the added salt increases the yield, and ways to scale up the process are under investigation. Since electrospray can be carried out under various conditions, e.g., in gases other than N_2 and at pressures under 1 atm, it should be feasible to apply the method to the preparation of various nanophase materials, including composites.

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Registry No. TiO_2, 13463-67-7; $Ti(OPr^i)_3$ acac, 15701-48-1; NH_4OAc, 631-61-8.

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[19] McClune, W. F., Ed. Powder Diffraction File, Set 21, JCPDS Int. Center for Diff. Data, Swathmore, PA, 1980, card 21-1272.

Second Harmonic Generation in Inorganic–Organic Complexes. 1. Control of Bulk Dipolar Alignment of *p*-Nitroaniline Crystal upon Complexing with Hydrobromic Acid

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Recently, much attention has been attracted to organic or inorganic molecular crystals with nonlinear optical properties because of their availability as practical materials.[1–5] For a material to exhibit second harmonic generation (SHG), it must have a noncentrosymmetric crystal

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[1] Levine, B. F. *Chem. Phys. Lett.* **1976,** *37,* 516.

[2] Tomaru, S.; Zembutsu, S.; Kawachi, M.; Kobayashi, M. *J. Chem. Soc., Chem. Commun.* **1984,** 1207.

[3] Wang, Y.; Eaton, D. F. *Chem. Phys. Lett.* **1985,** *120,* 441.

[4] Eaton, D. F.; Anderson, A. G.; Tam, W.; Wang, Y. *J. Am. Chem. Soc.* **1987,** *109,* 1886.

[5] Cox, S. D.; Gier, T. E.; Stucky, G. D. *Chem. Mater.* **1990,** *2,* 609.

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Table I. Intensities of Second Harmonic Generation of Inorganic Acid–Organic Complexes and Their Crystal Structures

complexes	SHG relative to urea	space group
*p*NA	0	$P2_1/n^a$
*p*NA·HBr	0.30 ± 0.02	*Fdd*2
*p*NA·HCl	0	$P2_1/n$
pNA·HNO_3	0	$P2_1/n$ or Pn^b
$(p\mathrm{NA})_2\cdot H_2SO_4$	0	
AN·HCl	trace	Cc^a

[a] The structures were confirmed by the powder XRD measurements. [b] The structure was solved with space group $P2_1/n$ or *Pn* (Figure D).

structure to accomplish the dipole alignment. Introduction of molecular asymmetry, chilarity, and hydrogen bonding, reduction of strength of dipole, changing counterions in organic or organometallic salts,[6] and making use of noncentrosymmetric rearrangements in centrosymmetric organic crystals[7] have been applied. At present, there are no suitable methods to control the crystal structure of organic molecules because of the polymorphism.[8] This paper gives the first example of the use of an *inorganic acid* to form nonlinear optical inorganic acid–organic complex crystals. The synthesis will develop one new route to the preparation of nonlinear optical materials.

p-Nitroaniline and aniline (AN) hydrochloric acid were commercially obtained from Wako Pure Chemical Industries, Ltd. Inorganic acid used was also commercially obtained. Inorganic acid–organic complexes were prepared as follows: *p*-Nitroaniline (1.2–1.4 g) was added to an aqueous solution of each acid (6 N, 20 cm^3) at 298 K, and the solution was kept at 278 or 298 K for 12–72 h. The resulting crystals were ground in a agate pestle for 10 min. The particle size of each sample was in the range 53–150 μm. The compounds were confirmed to be the *p*-nitroaniline acid complexes by the elemental analysis, infrared spectra, and ^{1}H NMR.[9] Hereafter, *p*-nitroaniline and *p*-nitroaniline hydrobromic acid, hydrochloric acid, nitric acid, and sulfuric acid complexes are abbreviated by *p*NA, *p*NA·HBr, *p*NA·HCl, pNA·HNO_3, and $(p\mathrm{NA})_2\cdot H_2SO_4$, respectively. No crystals were formed when hydrofluoric acid, hydroiodic acid, hexafluorophosphoric acid, phosphoric acid, and 12-tungstophosphoric acid were used as inorganic acids. The crystals obtained were used for X-ray crystallographic analysis as they were, except for $(p\mathrm{NA})_2\cdot H_2SO_4$ because of the low crystallinity. X-ray crystallographic data were collected on Rigaku AFC5R diffractometer, using graphite-monochromated Mo Kα radiation. Final *R* factors of *p*NA·HBr and *p*NA·HCl were 5.6 and 6.5%, respectively. (Crystallographic details of *p*NA·HBr and *p*NA·HCl were shown in Tables A and B and Tables C and D, respectively, in the supplementary material.)

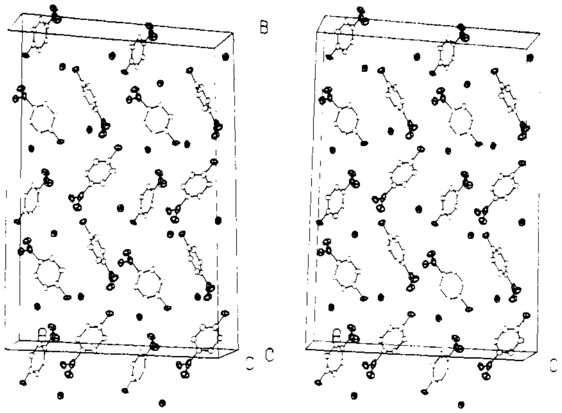

Figure 1. Stereoscopic view of the crystal packing of *p*NA·HBr (orthorhombic, *Fdd*2, *a* = 20.569 Å, *b* = 30.294 Å, *c* = 5.064 Å).

SHG measurements were carried out for powder samples (38 mg) by using a slightly modified method of Okamoto et al.[12] Urea (38 mg, 53–150 μm) was used as a reference material.[4] A Nd:YAG laser (Quanta-Ray, DCR-11) emitting at 1064 nm with 35 mJ/pulse was used in all experiments, and the frequency-doubled green beam at 532 nm was observed through bandpass filters. The data were well reproduced within ±10%. It was confirmed for *p*NA·HBr and *p*NA·HCl by the XRD and IR that no degradation of the samples occurred during the irradiation of the YAG laser beam and that the SHG intensity was proportional to (laser power)^2 (Figure B, supplementary material).

Table I shows relative intensities of SHG, compared to urea, for the series of complexes prepared. No SHG was observed for *p*NA, *p*NA·HCl, pNA·HNO_3, and $(p\mathrm{NA})_2\cdot H_2SO_4$. By contrast, SHG was observed for *p*NA·HBr and aniline hydrochloric acid (AN·HCl). The SHG intensity of *p*NA·HBr, 0.3 relative to urea, was the greatest among the samples in the present work although it was still lower than those of noncrystals of *p*NA in β-cyclodextrin (2–4 × urea) and deoxycholic acid (1 × urea).[4] Thus, the addition of inorganic acid, HBr, to *p*NA leads to the conversion of SHG-inactive *p*NA to the SHG-active complex. The excessively *p*NA loading to yield $(p\mathrm{NA})_{1.12}\cdot$HCl (by elemental analysis) by passing HCl gas through *p*NA-containing acetone solution (0.5 mol dm^{-3}) resulted in second harmonic generation (0.05 ± 0.01 relative to urea). This is a contrast to the fact that the stoichiometric complex of *p*NA·HCl was SHG inactive. It follows that appropriate addition of inorganic acid to a SHG inactive organic compound is one of the methods to make it SHG active although the addition of proton to the *p*NA molecule will decrease its polarization.

Crystal structures have been obtained for some of the composite solids as listed in Table I. The structures of SHG-inactive *p*NA·HCl and pNA·HNO_3 compounds were centrosymmetric (monoclinic, $P2_1/n$, *a* = 4.970 Å, *b* = 16.3065 Å, *c* = 9.323 Å, β = 93.89°; Tables C and D and Figure C, supplementary material) and centrosymmetric $P2_1/n$ or noncentrosymmetric *Pn* (Figure D), respectively, while it was reported that the structure of *p*NA·HCl is

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(6) Marder, S. R.; Perry, J. W.; Sahaefer, W. P. *Science* **1989**, *245*, 626; Calabrese, J. C.; Cheng, L-T.; Green, J. C.; Marder, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 7227.

(7) Weissbuch, I.; Lahav, M.; Leiserowitz, L.; Meredith, G. R.; Vankerzeele, H. *Chem. Mater.* **1989**, *1*, 114.

(8) Matsuoka, M. *Kagaku* **46**, 324 (1991).

(9) The infrared spectra of *p*NA·HCl, *p*NA·HBr, pNA·HNO_3, and $(p\mathrm{NA})_2\cdot H_2SO_4$ showed weak broad bands around 2000 cm^{-1}, as was reported for amino acid hydrochlorides[10] and aniline hydrochloric acid.[11] Strong broad bands appeared in the range 2000–3000 cm^{-1}, while the bands at 3480 and 3360 cm^{-1} due to the $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$, respectively, of *p*NA almost completely disappeared (Figure A). In ^{1}H NMR spectra of *p*NA·HCl, *p*NA·HBr, pNA·HNO_3, and $(p\mathrm{NA})_2\cdot H_2SO_4$, no lines due to H^+ at the nitrogen of amino group of *p*-nitroaniline were observed, probably because of the line broadening. Anal. Calcd for $C_6H_6N_2O_2$-(*p*NA): C, 52.17; H, 4.38; N, 20.29; O, 23.16. Found: C, 51.95; H, 4.32; N, 20.22. Anal. Calcd for $C_6H_6N_2O_2\cdot$HCl: C, 41.27; H, 4.04; N, 16.04; O, 18.34; Cl, 20.31. Found: *p*NA·HCl: C, 41.88; H, 4.03; N, 16.33; Cl, 19.70. Anal. Calcd for $C_6H_6N_2O_2\cdot$HBr: C, 32.90; H, 3.22; N, 12.79; O, 14.61; Br, 36.48. Found: C, 32.69; H, 3.18; N, 12.78; Br, 36.39. Anal. Calcd for $C_6H_6N_2O_2\cdot HNO_3$: C, 35.83; H, 3.51; N, 20.90; O, 39.76. Found: C, 35.98; H, 3.46; N, 20.92. Anal. Calcd for $(C_6H_6N_2O_2)_2\cdot H_2SO_4$: C, 38.50; H, 3.77; N, 14.97; O, 34.19; S, 8.57. Found: C, 37.51; H, 3.93; N, 14.62; S, 8.33.

(10) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; Vol. 1, p 66.

(11) Pouchert, C. J. *The Aldrich Library of FT-IR Spectra*; Aldrich Chemical Company: Milwaukee, 1985; Vol. 1, p 1189.

(12) Okamoto, N.; Abe, T.; Chen, D.; Fujimura, H.; Matsushima, R. *Opt. Commun.* **1990**, *74*, 421.

centrosymmetric $P2_1/c$.[13] The difference of the structure ($P2_1/c$ and $P2_1/n$) between pNA·HCl samples is probably due to the polymorphism and does not change the following discussion. The neighboring pNA·H$^+$ molecules in pNA·HCl crystal are packed alternately in an antiparallel alignment along *c* axis. Therefore, the pNA·HCl crystal is SHG inactive. In the *Pn* crystal structure of pNA·HNO$_3$, the dipoles of pNA·H$^+$ molecules are packed alternately in an antiparallel alignment along the *b* axis, and this compound is therefore SHG inactive, although *Pn* is a member of the polar space groups. The structure of the SHG-active pNA·HBr and AN·HCl were members of the polar space groups.

The structures of pNA·HBr is illustrated in Figure 1. pNA·HBr crystallizes in the orthorhombic space group *Fdd*2 consisting of pNA·H$^+$ and Br$^-$ ions. There were 16 molecules per unit cell. pNA·H$^+$ molecules are not packed alternately in antiparallel alignment along the *a* axis; the angle between the dipoles of pNA·H$^+$ molecules along *a* axis was 151°. This is the reason the pNA·HBr crystal is SHG active.

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Registry No. pNa, 100-01-6; HBr, 10035-10-6; pNa·HBr, 29084-75-1.

Supplementary Material Available: Crystallographic data for pNA·HBr (Table A), X-ray data collection and structure refinement of pNA·HBr (Table B), crystallographic data for pNA·HCl (Table C), X-ray data collection and structure refinement of pNA·HCl (Table D), infrared spectra of pNA, pNA·HCl, pNA·HBr, pNA·HNO$_3$, and $(p\mathrm{NA})_2\cdot\mathrm{H_2SO_4}$ (Figure A), dependencies of SHG intensities of pNA·HBr on laser power (Figure B), structure of pNA·HCl (Figure C), and possible structure of pNA·HNO$_3$ (Figure D) (10 pages). Ordering information is given on any current masthead page.

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[13] Sørensen, G. P.; Anderson, E. K. *Acta Crystallogr.* 1982, *B38*, 671.

Composition and Morphology of the Magnetic Reaction Product of 1,1'-Diacetylferrocene and *p*-Phenylenediamine. Caveat Emptor

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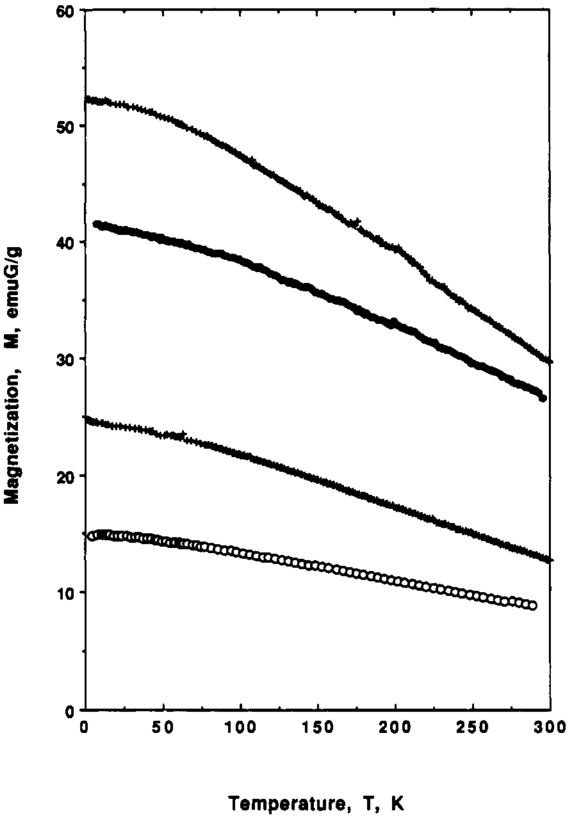

Figure 1. Magnetization as a function of temperature, *M*(*T*), at 19 500 G for **2** (+) and **3** (○) plotted along with the 50 000-G data reported in ref 4 (●).

The search for ferromagnetic behavior in polymeric materials is a focus of contemporary research.[1,2] Reports of ferromagnetic polymeric materials, however, have been plagued by ill-defined compositions, low yields, lack of characterization, and poor reproducibility.[3] Recently Zhao et al.[4] reported an ambient temperature, stable organometallic ferromagnet formed from the reaction of the reaction product of 1,1'-diacetylferrocene and *p*-phenylenediamine with cadmium acetate. Herein, we describe composition, morphology, and magnetic properties of this magnetic material.

Zhao et al. report the formation of $\mathrm{Cd_2Fe_2C_{36}H_{38}N_4O_4}$ (**1**)[5] which results from the addition of $\mathrm{Cd(O_2CMe)_2{\cdot}H_2O}$ to an *n*-amyl alcohol solution of 1:1 1,1'-diacetylferrocene and *p*-phenylenediamine which has been heated to reflux for 6 h. The resulting black precipitate was reported to be a ferromagnet at room temperature. We have repeated this synthesis with the following modifications: a commercially available sample (Aldrich) of 1,1'-diacetylferrocene was recrystallized from hexane prior to use, and commercial $\mathrm{Cd(O_2CMe)_2{\cdot}2H_2O}$ (Aldrich) was used instead of the monohydrate. *n*-Amyl alcohol (EN) was dried and

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† Contribution 6116.

(1) Proceedings on the Conference on Ferromagnetic and High Spin Molecular Based Materials. Miller, J. S., Dougherty, D. A., Eds.; *Mol. Cryst., Liq. Cryst.* 1989, *176*. Proceedings on the Conference on Molecular Magnetic Materials. Kahn, O., Gatteschi, D., Miller, J. S., Palacio, F., Eds. *NATO ARW Mol. Magn. Mater.* 1991, E198.

(2) Buchachenko, A. L. *Russ. Chem. Rev.* 1990, *59*, 307; *Usp. Khim.* 1990, *59*, 529. Kahn, O. *Struct. Bond.* 1987, *68*, 89. Kahn, O.; Journaux, Y. In press. Caneschi, A.; Gatteschi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* 1989, *22*, 392. Dulog, L. *Nachr. Chem. Tech. Lab.* 1990, *38*, 448. Ishida, H. *Encyl. Polym. Sci. Eng.* (*Supp. Vol.*) 1989, S446. Sugawara, T. *Yuki Gos. Kag.* 1989, *47*, 306. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* 1988, *88*, 201. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Acc. Chem. Res.* 1988, *21*, 114. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Science* 1988, *240*, 40. Miller, J. S.; Epstein, A. J. *New Aspects of Organic Chemistry*; Yoshida, Z., Shiba, T., Ohsiro, Y., Eds.; VCH Publishers: New York, 1989; p 237.

(3) Miller, J. S. *Adv. Mater.*, in press.

(4) Zhao Min-Guang; Lin Zhan-Ru; Ni Xuming *J. Phys. Condens. Matter* 1991, *3*, 6695.

(5) Zhao et al. report that this material may be denoted by $\mathrm{Cd_2Fe_2C_{12}H_{10}N_2O_7}$, i.e., %C = 22.85, %H = 1.60, %N = 4.44, %O = 17.76, %Fe = 17.71, %Cd = 35.64 vs %C = 46.63, %H = 4.13, %N = 6.04, %O = 6.90, %Fe = 12.05, %Cd = 24.25 for $\mathrm{Cd_2Fe_2C_{36}H_{38}N_4O_4}$.

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