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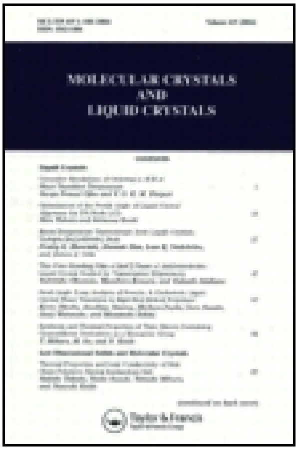

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Organic Semiconductors: Purification and Crystal Growth

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Organic Semiconductors: Purification and Crystal Growth

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First, a brief overview is given on literature dealing with purification, purity assessment, and crystal growth methods which are applicable to organic photoconductors and semiconductors under the aspect of the required high purity. Then some recent examples are presented of purification, material handling and crystal growth of some selected compounds (perylene, naphthalene, phenanthrene, TTF:chloranil and bipyridylammonium: $(TCNQ)_2$). Progress is reflected in greatly improved electrical properties of these materials which allowed detection of entirely new features, such as enhanced charge carrier scattering at phase transitions and non-Ohmic transport. Finally, some advanced crystal growth techniques are presented: Czochralski growth of organic molecular crystals under high purity conditions, flux growth of donor:acceptor crystals from a melt solution in one of the two components, oriented epitaxial growth "organic on organic" and epitaxial growth of organic materials on inorganic substrates.

OVERVIEW

The growth and perfection of single crystals of the archetype of an organic photo[1]- and semiconductor,[2] anthracene, has been studied in the early days by Huber (1949),[3] Mette and Pick (1953),[4] Sangster (1956),[5] Lipsett (1957, 1958),[6] Sherwood and Thomson (1960)[7] and Nakada (1961).[8] Similar investigations were soon extended on a greater variety of organic photo- and semiconductors. The activities before 1980 have been described in a review article by the author.[9] A number of original papers and review articles which appeared thereafter may be found in the references.[9-19] Very recently the techniques of melt crystallization (fractional crystallization, zone refining and crystal growth) have been treated in an exceptionally comprehensive way by Sloan and McGhie.[20]

In early photoconduction work by Hoesterey and Letson,[21] Oyama and Nakada,[22] Schmillen and Falter[23] and Probst and Karl[24] with tetracene-doped anthracene it has clearly been established that ppm (10^{-6} mol/mol) and even sub-ppm traces of chemical impurities can deteriorate the macroscopically observable transport properties (electron and hole drift mobilities, μ^- and μ^+) in a very drastic way so that a thermally activated ("multiple shallow trapping limited") transport arises with small effective mobilities, obscuring the much larger true "microscopic" mobilities, which follow, e.g. a $\mu \sim T^{-1.5}$ dependence. When trap depths are greater than approximately 0.6 eV, room temperature transport becomes too slow for pulsed time-of-flight observations[24] and these states are better classified as deep trapping centers.

From these experiments the need of achieving a level of purity, that hitherto never came into question among organic chemists or material scientists, was clearly established. Physical crystal perfection, besides the absence of chemical defects, was another aspect which became important as soon as the chemical impurity level was sufficiently down, cf. Reference 33.

Ultrapurification and ppm trace analysis of organic compounds posed new problems which required a great deal of scrutinity, skillfulness and manpower of many materials scientists. Zone refining, invented by Pfann[25] (1952), was soon applied to organic substances (Wolf 1954[26]; see also References 9, 20 and 27–29). But even this very efficient repetitive purification method required careful pretreatment of the starting material in special cases (e.g. chemical reactions chosen so as to transform certain persistent impurities with unfavorable distribution coefficients into more favorable derivatives, but leaving the main component unaffected); see e.g. References 9 and 30.

Analytical methods for the detection of trace amounts of molecules chemically related to the main component (matrix), which frequently constitute the major fraction of the impurities of organic compounds, are scarce. Gas chromatography can reach the 1 ppm level for molecules fairly similar to those of the matrix,[31] if these can be separated on a classical packed column. High resolution (capillary) gas chromatography, offering high separation power for even very similar molecules, on the other hand, scarcely reaches the 10–100 ppm level. Mass spectrometry can conveniently be used to identify the chemical nature of the molecules responsible for a certain gaschromatogram impurity peak, cf. Reference 9; however, this is only feasible if the peak is not too small; studying the impure end of a zone refining tube, where the impurity under question has been concentrated, has frequently helped to solve the problem. Other trace analytical methods are prompt and delayed (impurity-induced) fluorescence at low temperature, approaching the 0.001 ppm level in favorable situations, see e.g. Reference 9. Photocurrent excitation spectroscopy, based on selective optical detrapping of charge carriers, can also reach this level.[32] Triplet (free) exciton lifetime, charge carrier lifetimes and effective mobilities (see above), are other sensitive and rather universal purity criteria, which are not selective, however, and therefore unable to give any information on the chemical nature of the trap-forming impurity.[9] Conventional analytical methods, such as elemental analysis, VIS and IR optical absorption spectroscopy, NMR, etc. are usually not sensitive enough to lead beyond the 1000 ppm range.

For crystal growth from highly purified materials, cf. Reference 9, methods based solely on a phase transition have been preferred which avoid addition of an auxiliary component (solvent, or flux medium): Directional solidification from the melt after Bridgman, performed in a sealed (evacuated) glass ampoule, has most frequently been used for compounds which display long time stability at the temperature of their melting point. Avoiding accidental overheating during material transfer and during sealing requires special attention. Sublimation growth in a sealed ampoule can not only lead to free-standing single crystals of higher perfection, dressed with many perfect natural faces, but is often the only alternative method, if a material is not thermally stable at its melting point or if a lower temperature modification is wanted. A special variant, plate sublimation, introduced by the author some time ago, cf. Reference 9, provides especially small temperature gradients everywhere in the system and has therefore proved very advantageous for the growth of stoichiometric two-component complexes, where the components otherwise tend to segregate.

In what follows, the author wishes to illustrate and further enrich this field by presenting some recent results obtained in his group.

SOME RECENT RESULTS

The preparative steps for a typical time-of-flight photoconductivity experiment are displayed in Figure 1 which is self explanatory. Descriptions of extensive prepurification of naphthalene (by treatment with molten potassium metal, among other steps) and for phenanthrene have been given in literature.[30,34] A demonstrative example of zone refining of naphthalene is given in Figure 2. On the left side of Figure 2 seven molten zones are on the "ingot" at the same time. By slowly (~ 10 mm/h) lowering the ampoule in the multi-heater-furnace (displayed in the right part of the figure) the molten zones were caused to travel upwards. Blue fluorescing anthracene has already concentrated at the upper end. On the right

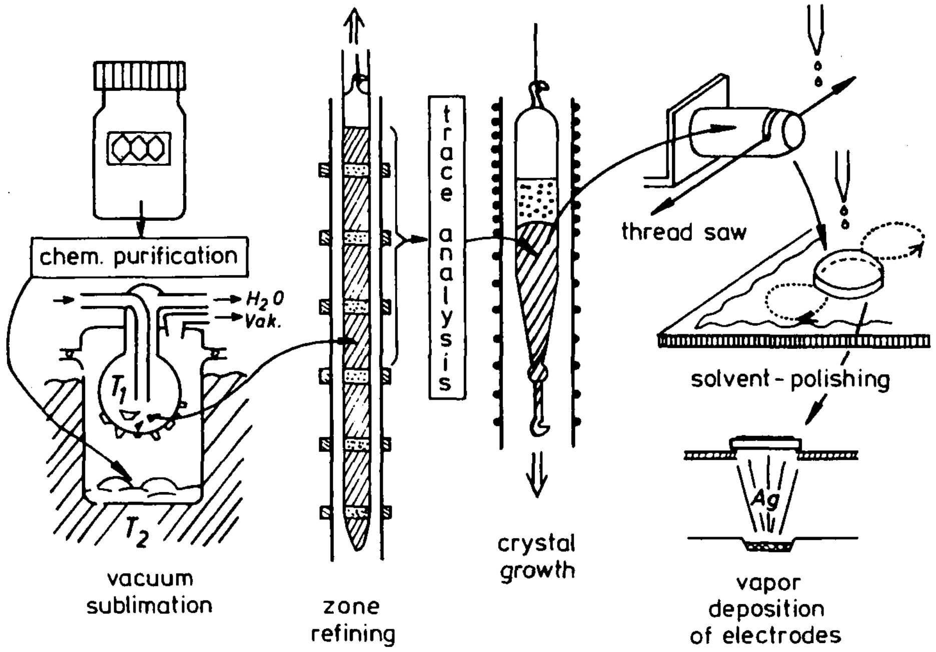


FIGURE 1 The typical steps for preparing high purity oriented single crystal slices for charge carrier time-of-flight measurements with organic photoconductors.

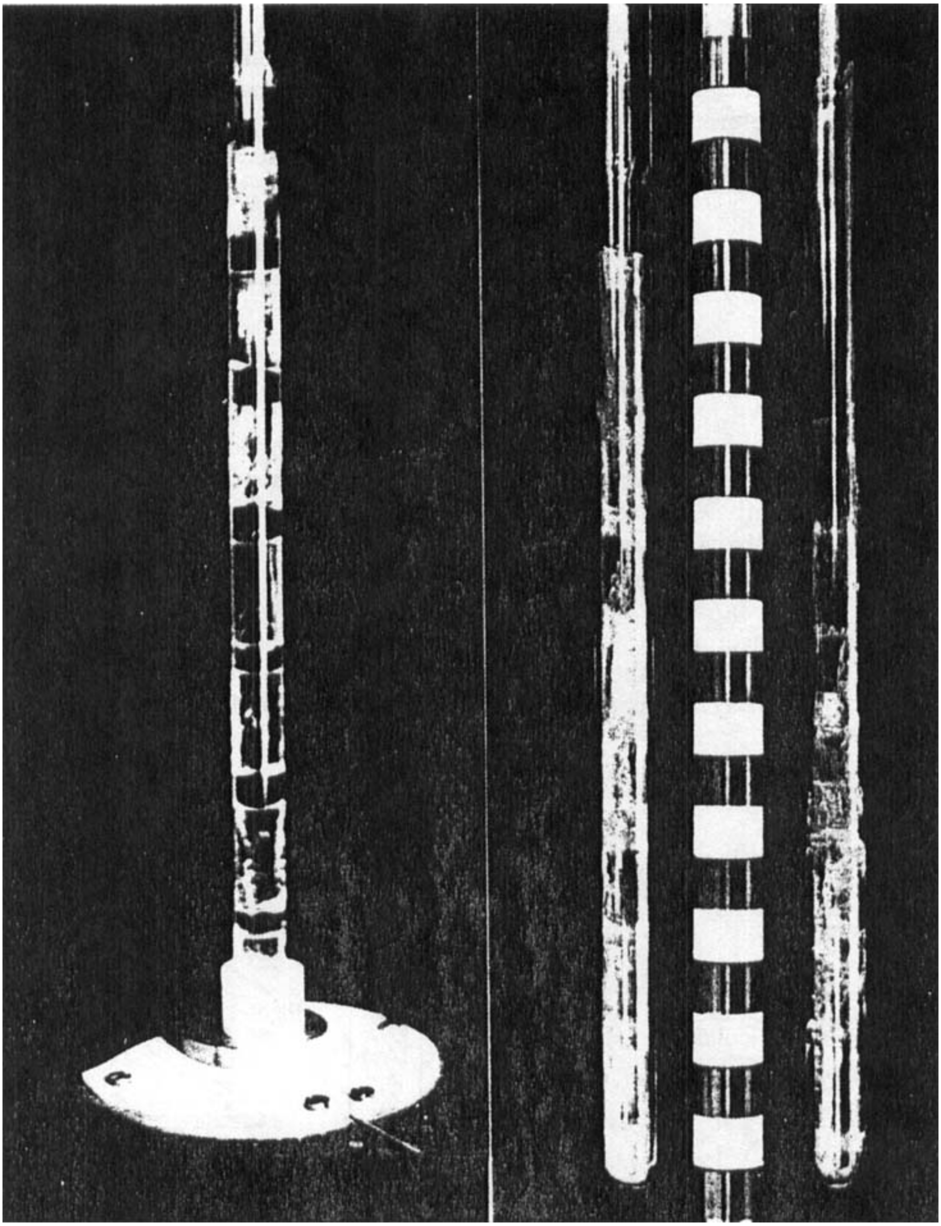


FIGURE 2 Zone refining of commercial "scintillation grade" naphthalene, left, and of naphthalene to which small amounts of azobenzene (yellow) and rhodamine B (red) had been added before zone refining for demonstration. The zone refining process has been interrupted after 10 zone passages.

See COLOR PLATE I.

side, two naphthalene tubes are displayed to which azobenzene (yellow) and rhodamine B (red) has been added before zone refining for demonstrating the accumulation in the molten zones (now solidified) and the gradual depletion (after 10 zone passages in the examples). For more details and for the kind of furnace used, the reader is referred to Reference 9. Sublimation transfer of individual fractions of ultrapurified organic material from a final zone refining tube to different storage ampoules—all equipped with vacuum break seals for further use—is displayed in Figure 3. The complete (evacuated) assembly is placed in a dry box heated to the appropriate sublimation temperature. A tap water-cooled sleeve is slipped over the ampoule, into which sublimation of the next fraction is wanted. That part of the zone refining tube, which is behind the wanted fraction, sticks out of the heat box or is cooled separately.

A cut and polished sample of a Bridgman-grown anthracene crystal is shown in Figure 4. A very perfect pyrene crystal, grown by the plate sublimation method, is displayed in Figure 5.

Phenanthrene has been known to exhibit anomalies in several of its physical properties between 340 and 350 K, where a phase transition occurs, cf. Figure 6. We have been able to study the hole mobility across the phase transition and found (on heating) a drastic decrease ($\mu \sim T^{-12}$), transition through a minimum and

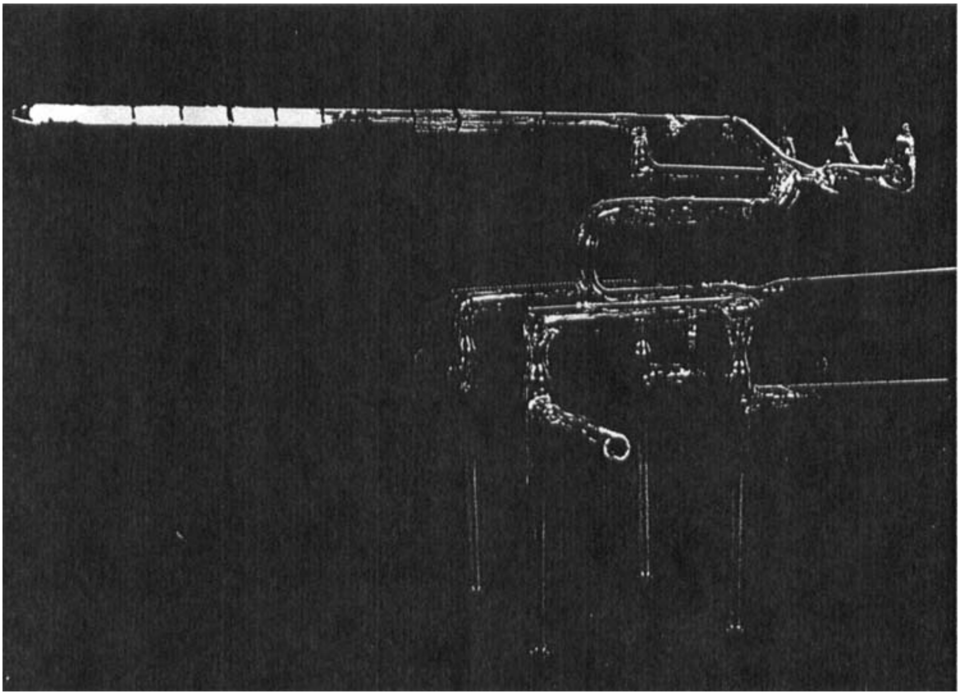


FIGURE 3 Glass assembly for transferring individual fractions of ultrapurified material by sublimation under vacuum from a zone refining tube to storage ampoules (or crystal growth ampoules).

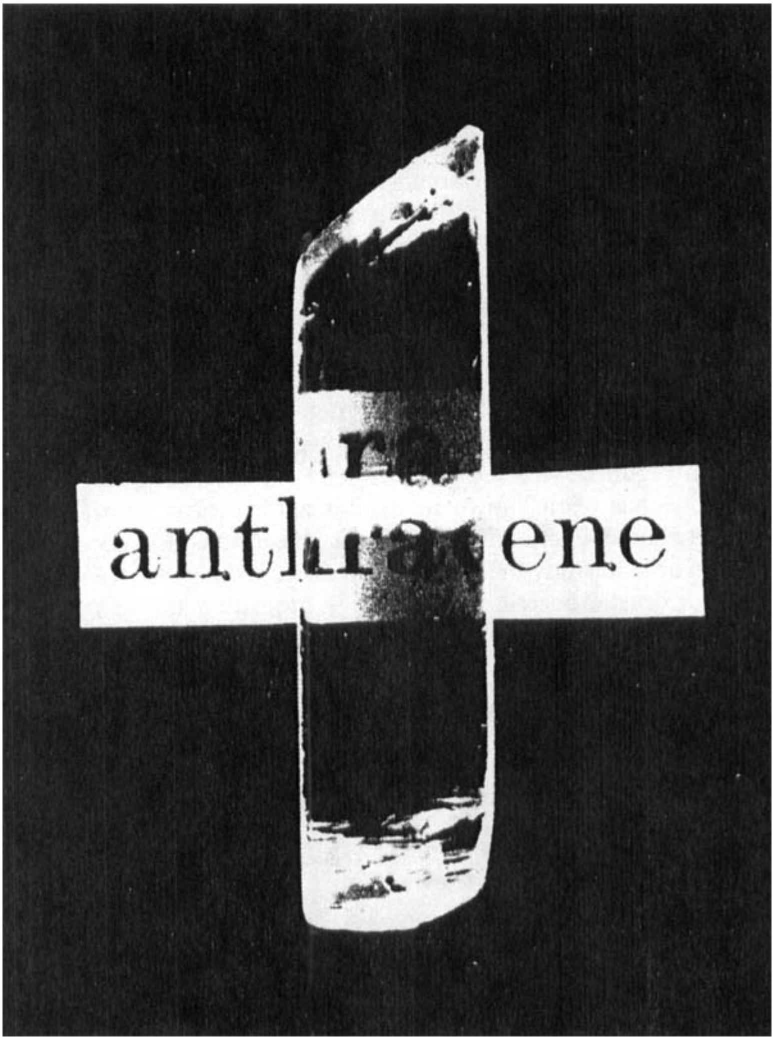


FIGURE 4 Cut and polished Bridgman-grown anthracene crystal, displaying its natural birefringence through 1 cm material (viewed approximately in c^*-direction). The length of the crystal is 2 cm.

See COLOR PLATE II.

increase (Figure 7) which obviously reflects the underlying lattice distortions and lattice dynamics. Laborious further purification (following essentially Reference 34) increased the hole mobility by more than one order of magnitude (Figure 8) as compared with the results of Figure 7 and with below-phase-transition mobilities published elsewhere.[35]

Naphthalene was the first organic photoconductor, for which charge carrier mobilities could be measured down to liquid He temperature,[30] see Figure 9. This was only possible after a number of steps of different purification methods, as

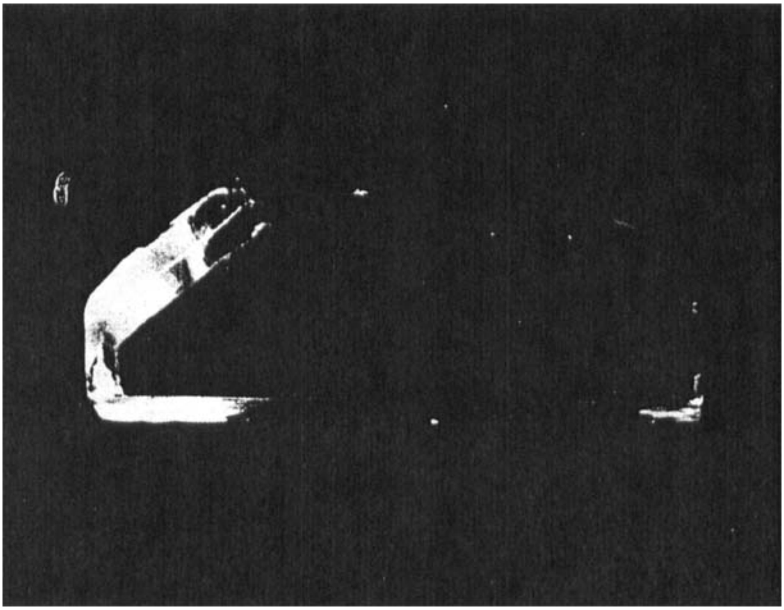


FIGURE 5 A pyrene crystal grown by the plate sublimation method; long dimension: 9 mm. See COLOR PLATE III.

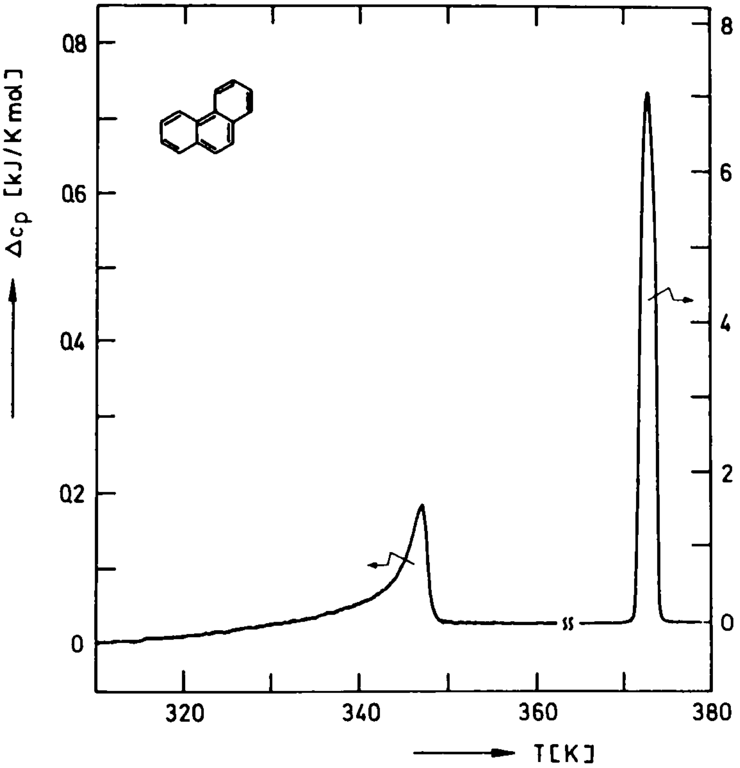


FIGURE 6 The specific heat curve of phenanthrene displays a higher order phase transition at 346.5 K (melting point is 371.5 K).—DSC measurements with zone refined phenanthrene.[37]

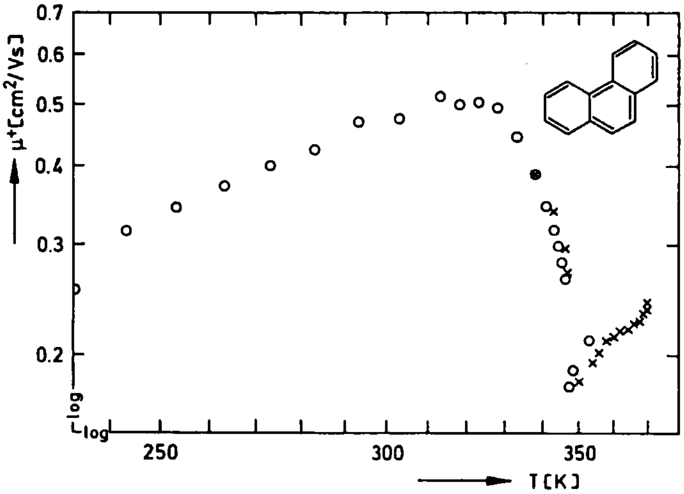


FIGURE 7 Phenanthrene, hole mobility versus temperature, log/log plot; zone refined material of medium purity. On heating the mobility decreases drastically near the phase transition, goes through a minimum and then rises again.[36a]

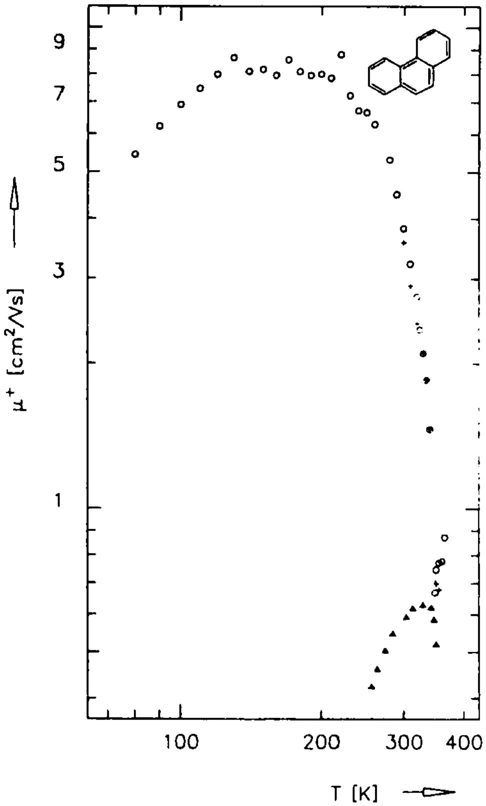


FIGURE 8 Phenanthrene, hole mobility versus temperature, log/log plot, for the electric field parallel to the crystallographic *a* direction; results obtained with extensively purified material (open circles)[37] are compared with literature data[35] (solid triangles).

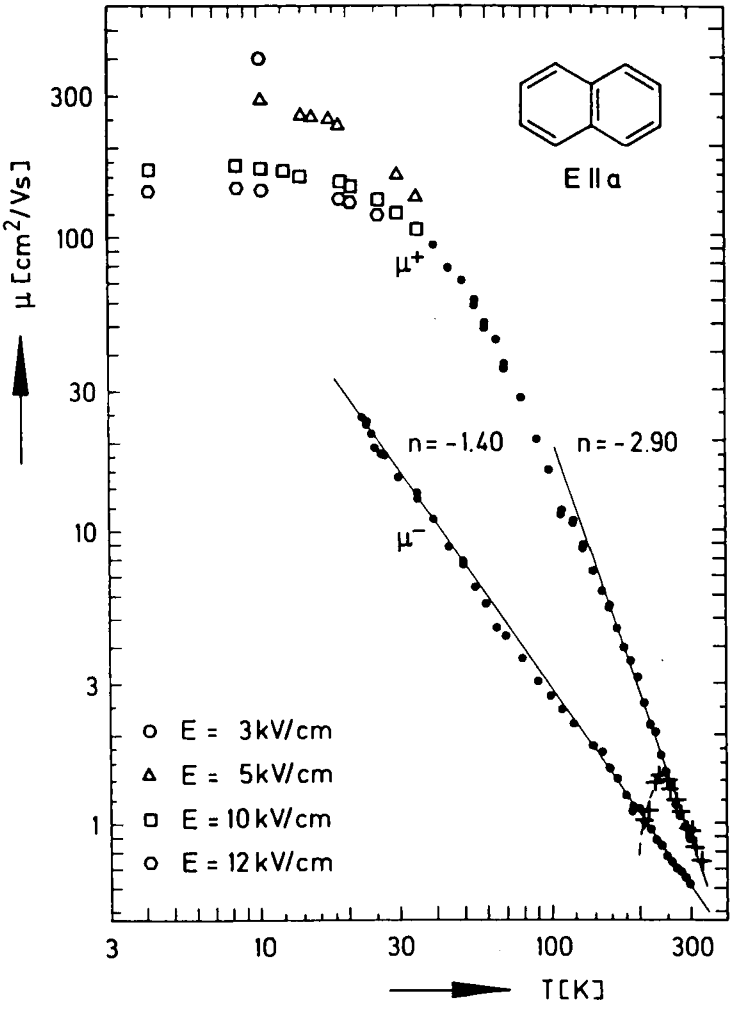
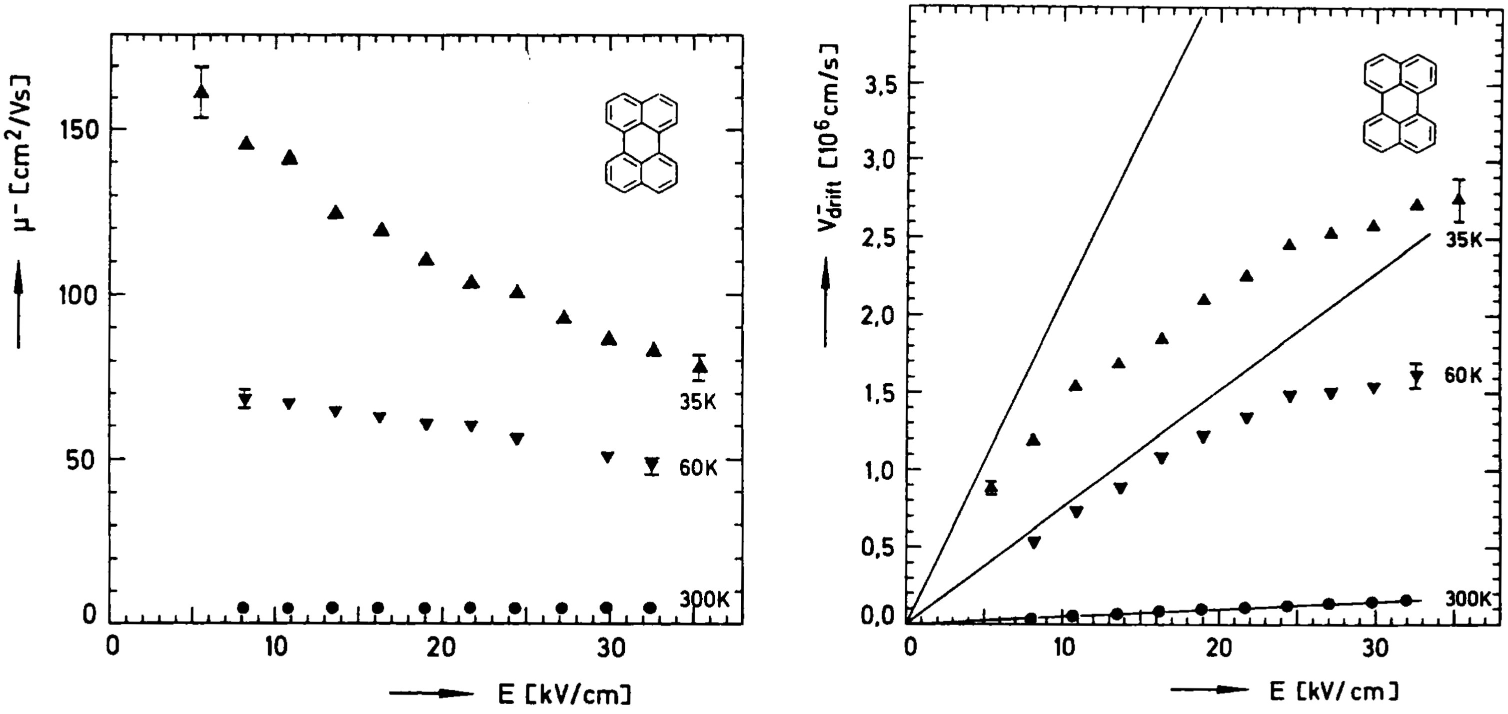


FIGURE 9 Naphthalene (ultrapurified), electron and hole mobility versus temperature, log/log plot, for the electric field parallel to the crystallographic *a* axis.[30] The comparatively high low-temperature hole mobilities were found to be electric field dependent, reflecting saturation of the drift velocities. For illustrating the progress with purification, earlier literature results[38] are indicated (in the lower right corner) by crosses.

described in Reference 30, and required special cutting, annealing and handling techniques of the samples.[33] The highest actually measured electron mobility was μ_{aa} = 400 cm^2/Vs at 3 kV/cm. These unexpectedly high low-temperature (electron- and hole-, cf. Reference 36 a,b,) mobilities turned out to decrease with increasing electric field, reflecting a tendency of the underlying carrier velocities to saturate; because a certain minimum field was necessary to detect the time-of-flight pulses, the $E \rightarrow 0$ mobilities could not be measured; these are obviously still much higher! The progress reached by ultrapurification can be judged from a comparison of these data with literature results,[38] indicated in Figure 9 as crosses.



(a) (b)

FIGURE 10 a) Perylene (ultrapurified), electron mobility versus electric field at 300, 60 and 35 K. The low-temperature mobility decreases with increasing field. Crystal orientation: $\sphericalangle\,(n,a) = 90°$, $\sphericalangle\,(n,b) = 29°$, $\sphericalangle\,(n,c^*) = 61°$, where n is the normal to the crystal slice, thickness $d = 368\ \mu m$, $\Delta d/d = 2.7\%$; b) same data, but plotted as electron velocity versus electric field.

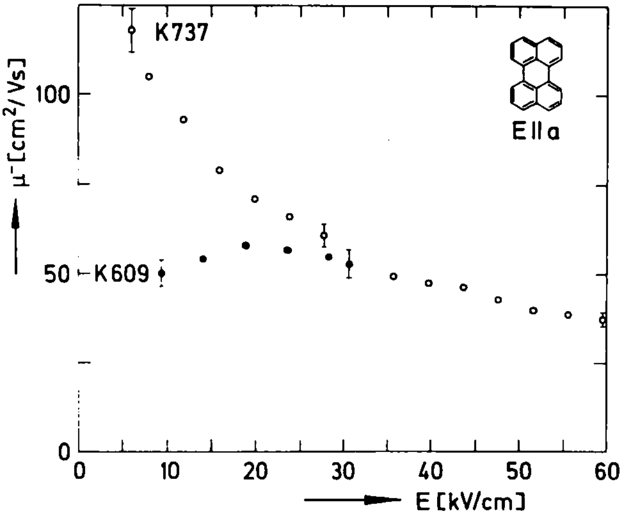


FIGURE 11 Perylene, field dependent electron mobility at 25 K in an ultrapure sample (K737), and in a sample in which low-field transport is still influenced by multiple shallow trapping (K609). Crystal orientation: *n*‖*a*‖*E*.

Perylene proved to be a much better model compound for organic photoconduction than anthracene, because it can be purified with less effort (only vacuum sublimation and several multipass zone refining steps with ~100 zone passages each are required), and it tends to form good quality Bridgman crystals, even when highly purified. Microscopic electron mobilities could be detected down to ~30 K. High mobilities in conjunction with non-Ohmic transport were observed in this material too.[30,36a,b;39] An example is given in Figure 10a. These data are replotted in Figure 10b as electron velocity versus electric field; the straight lines represent (approximate) tangents to the low field velocities; their slope reflects the low-field mobilities (4.3, 76, and 210 cm^2/Vs at 300, 60, and 35 K, respectively). In less extensively zone refined perylene, Figure 11 (solid dots, sample K609), a field dependent multiple shallow trapping/detrapping transport behaviour is observed, and only the high field data approach those of the purer sample. This is a unique demonstration of a field-assisted Poole-Frenkel type of detrapping.[39]

Crystal growth by plate sublimation has been used successfully (see also Reference 40) to prepare bulky single cyrstals of several mm^3 volume of the semiconducting mixed-stack type charge transfer complex tetrathiafulvalene:chloranil (TTF:CA), which displays a phase transition at 84 K, at which the degree of charge transfer changes from ~30 to ~70%.[41] The (zero pressure) dc-conductivity, obtained with one of these samples is plotted in an Arrhenius representation in Figure 12. Single crystals of up to ~1 × 1 × 8 mm^3 of the radical ion salt 2,2'-bipyridylammonium:(TCNQ)$_2$[42] could also be obtained by plate sublimation. This is a rare example of sublimation growth of an ionic organic complex with metallic-like electrical conductivity at room temperature, see Figure 13.

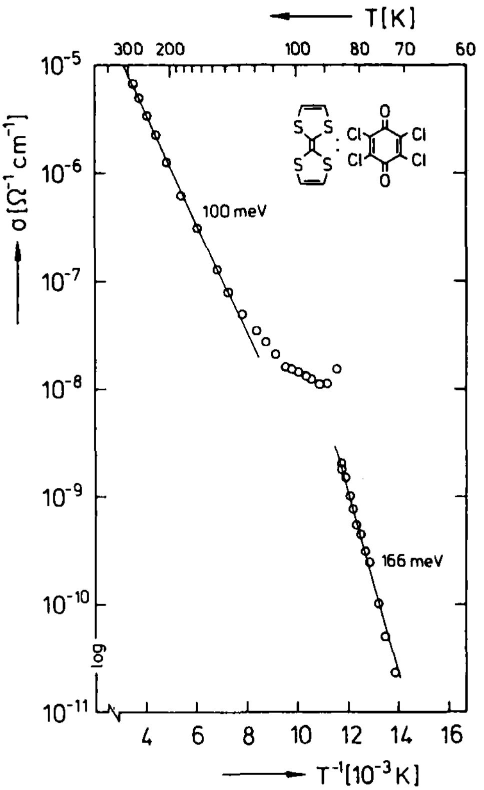


FIGURE 12 TTF:Chloranil, electric conductivity of a sublimation grown single cyrstal versus reciprocal temperature.

ADVANCED TECHNIQUES

Czochralski and Nacken-Kyropoulos growth, i.e. growth from the melt by immersing a cooled seed which is subsequently slowly pulled out or left stationary, are not unproblematic with organic molecular crystals, because of the non-negligible vapor pressure of typical compounds which might be of interest. Not only are closed systems required, but problems would also be expected to arise from parasitic seeding from the vapor phase. Bleay, Hooper, Narang, and Sherwood[43] and later Klapper and coworkers[12,17] demonstrated that these difficulties can be overcome at least with such organic compounds which combine a sufficiently high molecular weight with a comparatively low melting point, such as e.g. benzophenone ($C_{13}H_{10}O$, m.p. 48°C). For Czochralski growth of organic crystals from ultrapurified material with, at the same time, higher melting points and (therefore) higher vapor pressure, special requirements had to be met: A high-vacuum-tight growth apparatus[44] was built up from glass and stainless steel, equipped with (ultrahigh vacuum-tight) transmission of rotational and (precision) translational motion, and heated in such

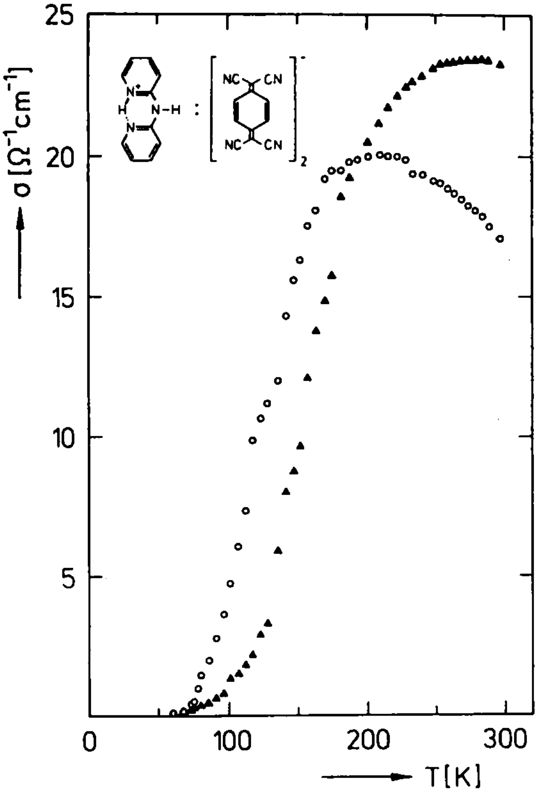
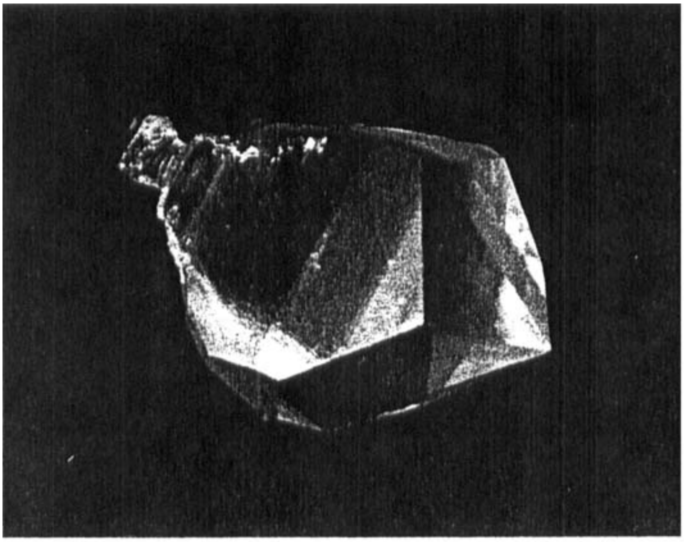


FIGURE 13 2,2'-Bipyridylammonium: $(TCNQ)_2^-$, electric conductivity of two sublimation-grown single crystals along the elongated crystal direction.

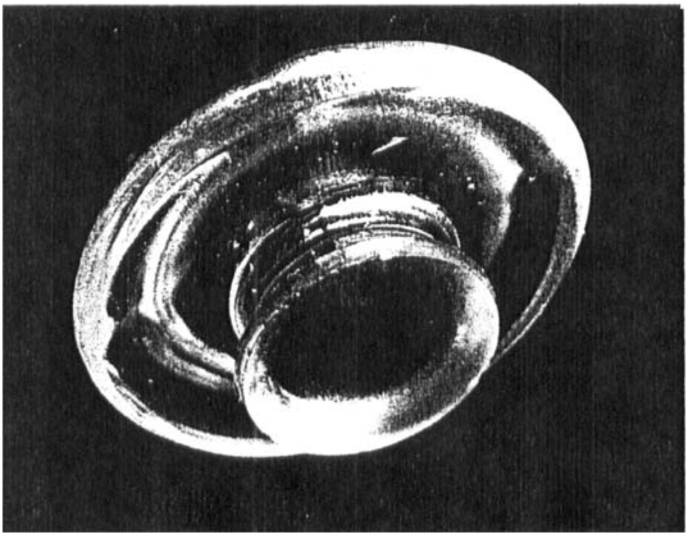
a way that condensation from the vapor phase was prevented at all parts. Figure 14a gives an example of a benzophenone crystal so obtained; Figure 14b of a pyrene crystal ($C_{16}H_{10}$, m.p. 156°C).

Flux growth does not seem to have been used for organic crystals, although common in the inorganic semiconductor field (e.g. growth of III-V semiconductors from the group III—metal-rich melt at temperatures much below the melting point of the compound). Since the auxiliary component is part of the compound in these cases, the only (chemical) defects it can cause are stoichiometry defects. Along these lines we have been able to grow bulky crystals of the donor:acceptor complex naphthalene:pyromellithic-dianhydride (N:PMDA) from a naphthalene-rich melt by cooling. In a similar way 2,3-dimethylnaphthalene:tetracyanobenzene crystal needles could be obtained at the naphthalene-rich end of the phase diagram of these components (see Figure 15[45]) at a sufficiently low temperature to keep the acceptor of this complex, TCNB, stable, whereas it gradually decomposes at the melting point of the complex.

Epitaxial growth is another crystal growth method for which experience is essentially lacking in the organic field. The more trivial case is homoepitaxy (substrate



(a)



(b)

FIGURE 14 a) Benzophenone, b) pyrene; single crystals obtained by Czochralski growth under high purity conditions; scale is in cm and applies to both figures.

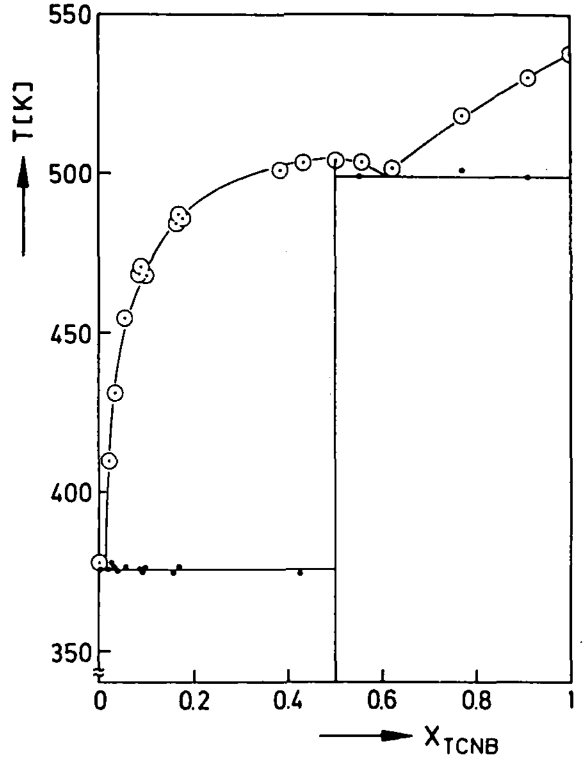
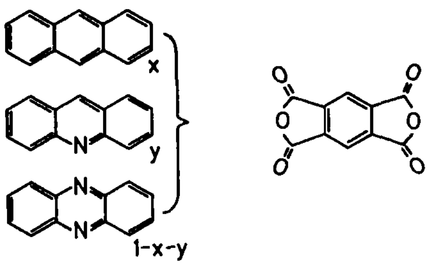
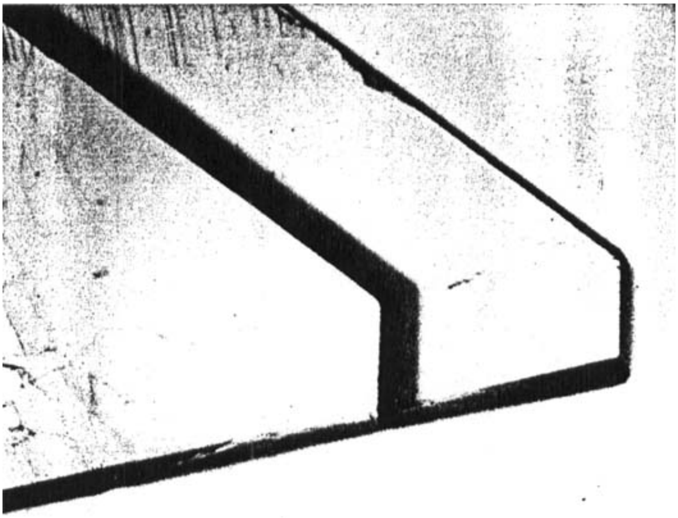


FIGURE 15 2,3-Dimethylnaphthalene-tetracyanobenzene (2,3-DMN-TCNB), phase diagram, measured by differential scanning calorimetry on a Perkin-Elmer DSC-2. Low temperature flux crystal growth of the 1:1 donor:acceptor complex 2,3-DMN:TCNB is possible at the left side of the phase diagram by slow directional cooling.

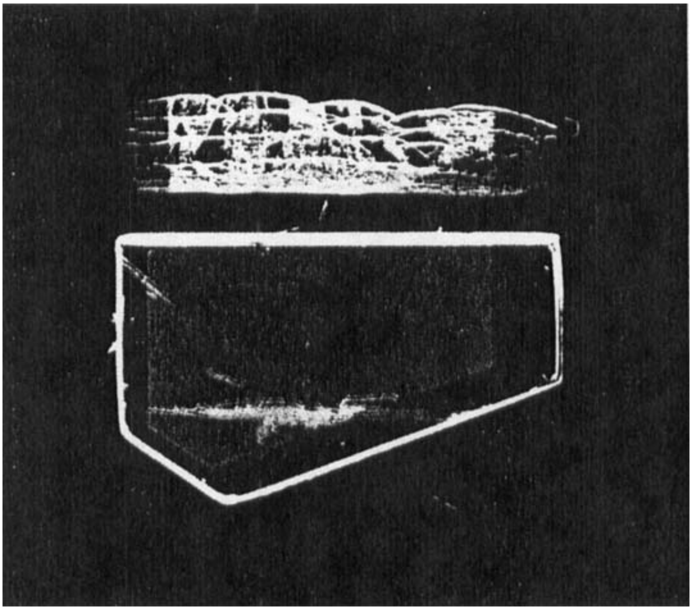
crystal and overlayer are chemically and crystallographically the same, but undoped and doped; or differently doped; or isotopically substituted, e.g. deuterated, and undeuterated). Examples are displayed in Figures 16a and 16b. These crystals were made by the plate sublimation technique in a special ampoule which has been described elsewhere.[9] Heteroepitaxy demands, among other conditions, a rather careful match between the two crystal lattices in question. A ternary phase diagram of three isomorphic stoichiometric donor:acceptor complexes,[46] anthracene:PMDA, acridine:PMDA and phenazine:PMDA,



displaying complete miscibility, cf. Figure 17, has been used for basic investiga-

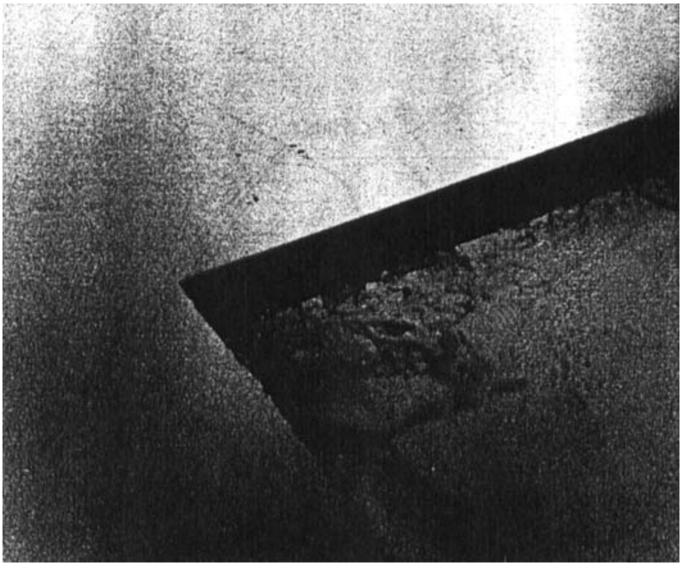


See COLOR PLATE IV. (a)

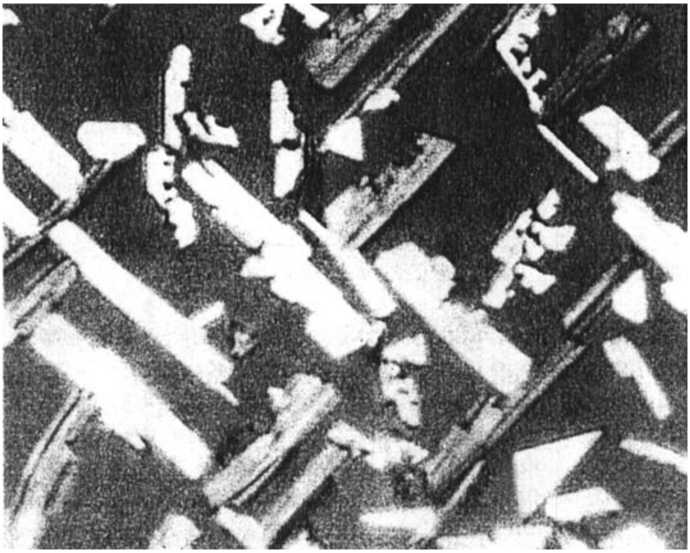


See COLOR PLATE V. (b)

FIGURE 16 Epitaxial growth of organic crystals from the vapor phase: a) homoepitaxy of blue-violet benz[f]azulene-doped anthracene on undoped anthracene continued by undoped anthracene; (the coloured ribbon goes all through the crystal slice, cf. Reference 9). b) Homoepitaxy of a surface layer of tetracene-doped anthracene (green fluorescence) onto a concave surface of an undoped anthracene cyrstal (blue fluorescence); the epitaxial layer is several tenths of a mm thick, as can be seen from the cleaved-off (crumbled) lamella. c) Heteroepitaxy of (red) anthracene:PMDA on (yellow) phenazine: PMDA; this crystal has been cleaved for demonstration. d) Organic on inorganic heteroepitaxy of PTCDA on NaCl(001). The horizontal figure edge is approximately 2 mm in a), 8 mm in b), 5 mm in c), and 0.3 mm in c).



See COLOR PLATE VI. (c)



See COLOR PLATE VII. (d)

FIGURE 16 (*cont'd*)

tions.[47] Epitaxial growth of anthracene:PMDA on phenazine:PMDA is demonstrated in Figure 16c with a crystal, cleaved afterwards. These are promising systems for studying charge separation in the primary step of photoconduction.

Finally, heteroepitaxial growth of organic photo- and dark-conductors on inorganic substrates constitutes a very promising new field: If organic crystals can play

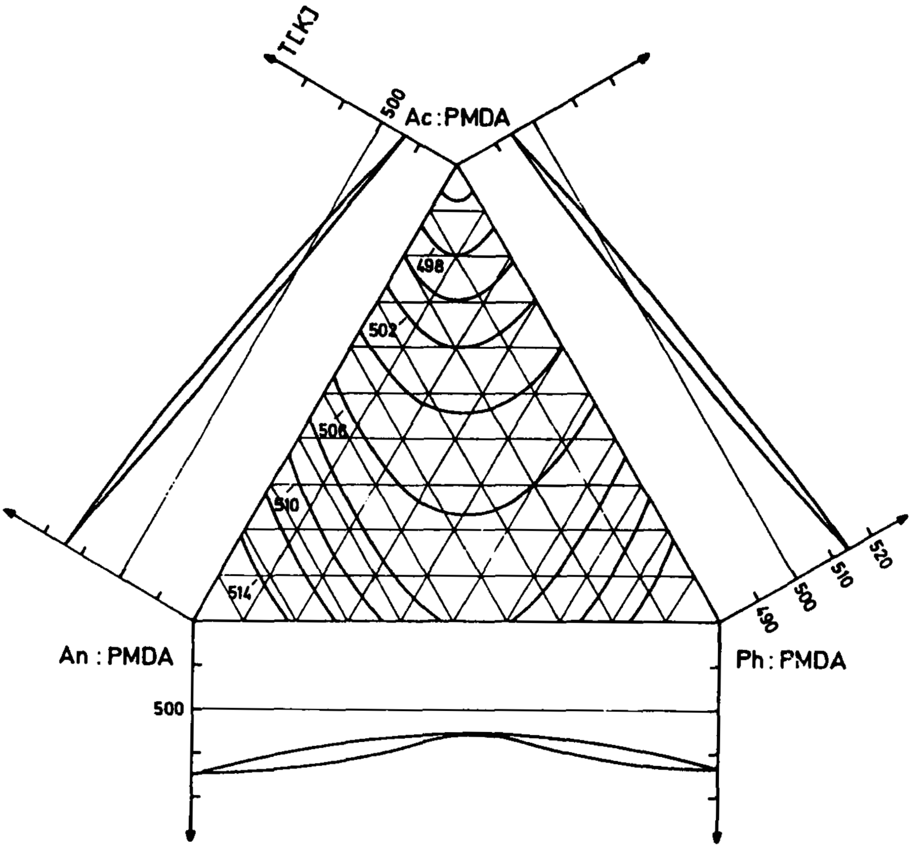
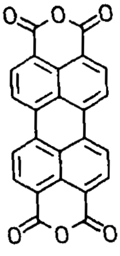


FIGURE 17 The ternary phase diagram of (anthracene$_x$-acridine$_y$-phenazine$_{1-x-y}$): PMDA (for clarity the solidus lines have been omitted in the ternary triangle).[46]

a role in electronics—some recent results mentioned in this article and others which could not be addressed here, lend support to this idea—then hybrid organic on inorganic microstructured devices are very likely to be among the first candidates. It is therefore desirable that progress be made with clarifying the basic principles governing organic (van der Waals-bonded) crystal growth and interactions on main valence or ionically bonded inorganic semiconductor substrates. Such activities will require detailed investigations on well prepared and characterized surfaces. In a first step in this direction we have studied epitaxial growth of perylene-tetracarboxylic-dianhydride, PTCDA ($C_{24}O_6H_8$),



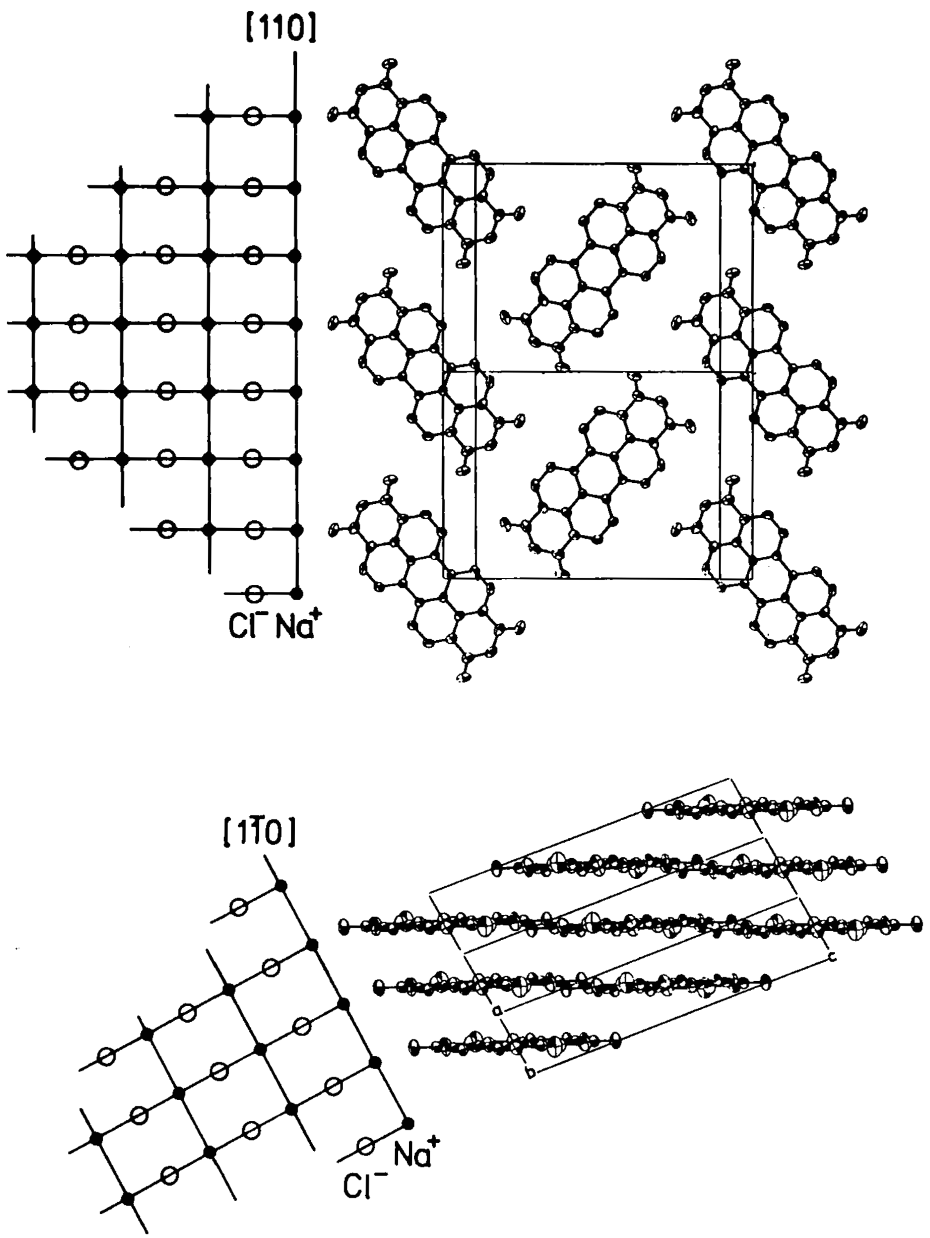


FIGURE 18 Epitaxial growth of PTCDA on NaCl, viewed parallel and perpendicular to the molecular stacking axis *a*. The PTCDA structure was plotted after the atomic coordinates which we kindly obained from Lovinger, Forrest, Kaplan, Schmidt, and Venkatesan, cf. *J. Appl. Phys.*, 55, 476 (1984).

on freshly cleaved sodium chloride faces. As can be seen from Figure 16d, oriented overgrowth occurs, however, due to the high symmetry of the substrate surface and the low (monoclinic) symmetry of the overlayer, in two (more precisely four) symmetry-degenerate orientations, namely with the PTCDA stacking direction *a* either parallel to $[110]_{NaCl}$ or parallel to $[1\bar{1}1]_{NaCl}$ (or antiparallel). This information was obtained independently from thin-film X-ray diffraction and from electron diffraction experiments in a 250 KeV electron microscope.[48] A model of the epitaxial relations is displayed in Figure 18. The relative lattice misfit for a_{PTCDA} is $6 \cdot 10^{-2}$, for b_{PTCDA} it amounts to 10^{-3}. Obviously the carbonyl oxygen atoms are in close contact to the sodium ions. Similar overgrowth behaviour was observed on silicon and on InP. For further progress to be made in this direction, detailed studies on well prepared and characterized surfaces will be necessary, a typical domain of ultrahigh vacuum surface physics.

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