

The Quest for D- σ -A Unimolecular Rectifiers and Related Topics in Molecular Electronics

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Progress is being made toward unimolecular devices, whose function relies on the manipulation of the energy levels or conformations of either a single molecule or a small cluster of molecules. These devices, at the forefront of “molecular electronics”, should leapfrog conventional microelectronics, for which a 100-Å lower limit in “design rules” is predicted. Fast organic rectifiers and transistors should be addressable by scanning tunneling microscopy. The quest for the proposed Aviram-Ratner D- σ -A unimolecular rectifier is reviewed, where D is a good one-electron donor (but poor acceptor), σ is a covalent, saturated “sigma” bridge, and A is a good one-electron acceptor (but poor donor). D- σ -A should more easily form the zwitterion $D^+-\sigma-A^-$ (followed by fast intramolecular electron transport $D^+-\sigma-A^- \rightarrow D-\sigma-A$) than the zwitterion $D^--\sigma-A^+$. Many candidate D- σ -A molecules form Langmuir-Blodgett films and Schottky barrier rectification have been seen, but intramolecular electron tunneling through D- σ -A has not yet been confirmed.

MOLECULAR ELECTRONICS (ME) (1) has two current definitions as follows.

1. the “wider” definition, which includes the interesting electrical behavior (conductivity, superconductivity, etc.) of all known lower dimensional systems, Langmuir-Blodgett (LB) films, and clusters
2. the “stricter and narrower” definition, which focuses on the properties of the single molecule

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This chapter presents these definitions, followed by a discussion of a few “bulk” molecular devices. The next sections present ideas for external connections to single molecules, several proposals for unimolecular electronic devices, and a review of efforts to harness intramolecular electron transfer.

The last two sections chronicle the progress made toward the realization of the organic rectifier, a proposal advanced in 1974 by Ari Aviram, Mark A. Ratner, and co-workers (2–4) that a single organic molecule of the type D– σ –A could be a rectifier of electrical current. This molecule D– σ –A would act as a rectifier, because the D end is a good organic one-electron donor (but poor acceptor), σ is a covalent saturated (“sigma”) bridge, and A is a good organic one-electron acceptor (but poor donor). The Organic Rectifier Project (ORP) at the Universities of Mississippi (1981–1991) and Alabama (1986–1991) has been the combined effort of a synthetic chemist (Charles A. Panetta) and a physical chemist (Robert M. Metzger) to put to a practical test the Aviram–Ratner Ansatz (5–34). The impetus for the ORP, one of the key experiments in ME, has been that the working thickness promised by such a D– σ –A device is of the order of one or two molecular lengths, that is, about 5 nm. The rosiest forecast is that a working length (“design rule”) of 100 Å = 10 nm is the smallest conceivable for silicon or gallium arsenide technology; present limits are well above 100 nm.

As discussed in the last section, the rectification by a single organic molecule or by an organized LB (35–41) monolayer of such molecules has not been achieved by the ORP. However, Sambles (University of Exeter) and co-workers have observed rectification by an LB monolayer (42, 43), but this is ascribed (44, 45) to a Schottky barrier rather than to the Aviram–Ratner mechanism (this is not surprising, given the specific D– σ –A and D⁺–π–A[−] molecules used). The revolutionary scanning tunneling microscope (STM) (46) shows promise for confirming the Aviram–Ratner Ansatz (22, 23, 31, 32), but difficulties exist in measuring currents through molecules in an unambiguous manner.

Broad and Narrow Definitions of Molecular Electronics

The term ME was popularized by the late Forrest L. Carter, who organized three international workshops on ME devices starting in 1981 (47–49); these were followed by similar conferences in Varna (50), Hawaii (51), and St. Thomas (52). In 1983, an unscientific proposal about self-assembling biological “computers” (“biochips”) received undeserved and uncritical worldwide media attention; the understandable reaction to such exaggerations almost drowned the infant field of ME! A very sobering note outlined what technical accomplishments were still needed (53, 54). Since then, more conservative chemists, physicists,

and materials scientists have broadened the definition of ME and relabeled some of their research areas as ME, and thus have restored respectability to the field.

At present, two interpretations of ME exist. In its first, broader, definition, ME encompasses the studies of all molecule-based electronic processes in lower dimensional systems, to wit, in approximate historical order:

- (A1) intercalated graphites (C_8K , etc.) (55)
- (A2) intercalated two-dimensional chalcogenides (TaS_2 , etc.) (56)
- (A3) charge-transfer salts (organic conductors and superconductors) (57)
- (A4) conducting low-dimensional polymers (57, 58)
- (A5) inorganic linear-chain compounds (59)
- (A6) LB multilayers (35–41)

These research areas have been studied worldwide for almost two decades, and relabeling them as ME may be a convenient shorthand, an attention-getting method for funding research proposals, or just a current fad.

In the second, more narrow definition, ME devices (“zero-dimensional devices”) utilize the electronic properties of single molecules or clusters. Examples of proposals are as follows:

- (B1) Aviram and Ratner’s rectifier, which is the main subject of this chapter (2–4)
- (B2) Aviram and Ratner’s hydrogen atom switch (3, 4)
- (B3) Mitani’s proton transfer system (60)
- (B4) Carter’s soliton switch (61)
- (B5) Fujihira’s LB monolayer photodiode (62)

The following proposals have been brought forth for “passive” molecular connectors that may one day be useful to interrogate unimolecular ME devices:

- (C1) molecular wires and antennas, for example, carotenes and other polyenes (63)
- (C2) Aviram’s linked thiophene “connects” (64) realized by Tour et al. (65)
- (C3) Miller’s “molecular lines” (66)
- (C4) molecular inclusions in urea, thiourea, cyclodextrins (67), calixarenes (68), or zeolites (69)

It is imperative that these potential devices utilize fast intramolecular electron transfer speeds (faster than 1 GHz, that is, electron per molecule

per nanosecond). Indeed, ME will enjoy a substantial margin over present-day semiconductor electronics only if ME can couple the advantages of molecular size (<2 nm) and fast intramolecular electron transfer (>1 GHz). There is little use in making a small but slow device.

Bulk Molecular Devices

First, we discuss some known “bulk” molecular devices, even though they are molecular devices only in the larger sense (i.e., because of the band structure of the solids or because of phase change properties or other bulk effects).

Bulk Organic Rectifiers. After the discovery of the *pn* junction diode (*p* is hole-rich region, *n* is electron-rich region) and the *npn* transistor, it was of interest to see whether macroscopic films of organic molecules could function as bulk *pn* rectifiers (diodes) or as *npn* transistors. The *pn* rectifiers would occur if a film or crystal of an organic electron donor (which becomes a *p* region) were brought in contact with that of an organic electron acceptor (*n* region). This was indeed verified in the 1960s (70).

Pockels–Langmuir, Langmuir–Blodgett, and Langmuir–Schaefer Films. Before discussing organic rectifiers based on LB films, we define (Figure 1) the terms Pockels–Langmuir (PL) (17), LB, and Langmuir–Schaefer (LS) films (37–39). The self-assembly of one-molecular thick “monolayers” at the air–water interface was studied scientifically by Agnes Pockels, Lord Rayleigh, and Irving Langmuir (39). PL films may be a convenient term (17) for stable self-assembling monolayers at the air–water interface (37) (Figure 1a). A few studies have used mercury as a subphase (71). Kathleen Blodgett found that PL monolayers could be transferred quantitatively to a solid substrate by dipping the substrate vertically through the PL monolayer. These monolayers are then LB monolayers or (by repeated dipping) LB multilayer films (35, 36) (Figure 1b and 1d). Schaefer found that horizontal dipping of a substrate could also transfer films that otherwise did not transfer well by the LB method. These are LS films (72) (Figure 1c).

An early study of electrical conductivity between an Al electrode and a mercury drop through *N* Y-type LB monolayers of cadmium arachidate [CA = Cd(C₁₉H₃₈COO)₂] (73), as a sandwich Al|(CA)_N|Hg (here, vertical bar denotes an interface), claimed that, beyond a background through-film current density j_d (due to defects), the intrinsic current density j_i depended upon the number of layers and followed the Bethe–Sommerfeld tunneling equation: $\log j_i \propto V^{1/2}$, where V is the tunneling barrier. There were other similar studies (74); groups in the United Kingdom found instead $\log j \propto V^{1/4}$, which favored an interpre-

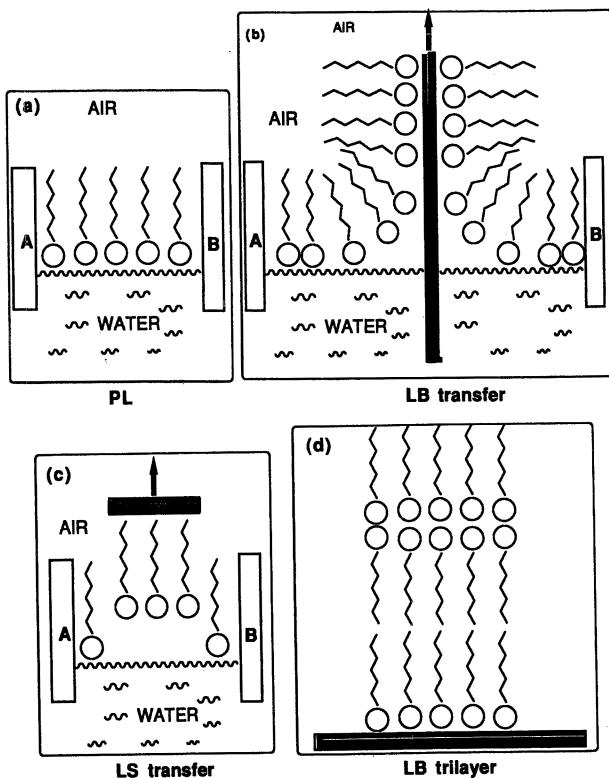


Figure 1. a, Structure of Pockels-Langmuir (PL) film at air–water interface; A and B are solid barriers that minimize the monolayer surface area (A_c) at the collapse surface pressure (Π_c); the tadpole-shaped structure represents an amphiphilic molecule: The circle is its polar “head” group; the zig-zag is its hydrophobic “greasy tail,” for example, a long saturated alkane chain. b, Vertical transfer of Langmuir-Blodgett (LB) film (35, 36) onto a hydrophilic solid substrate (e.g., Al). c, Horizontal transfer of Langmuir-Schaefter (LS) film (72) onto a hydrophobic solid substrate (e.g., graphite). d, Structure of LB Y-type trilayer on hydrophilic substrate.

tation of a defect-limited process (75, 76). Because they are somewhat disordered within the plane of the film, LB multilayers have more electrical defects than may be expected naively (77).

Multilayer Langmuir-Blodgett Organic Rectifiers. Kuhn and co-workers (78) showed that one can obtain a “pn” (or DA) rectifier in a LB multilayer sandwich $\text{Al} | (\text{CA-D})_q | (\text{CA})_r | (\text{CA-A})_s | \text{Al}$. Here $(\text{CA-D})_q$ denotes the electron-donor system D ($= q$ LB monolayers of CA randomly doped in the ratio 5:1 with suitable organic π -electron donors D), whereas $(\text{CA})_r$ denotes a spacer layer of r undoped monolayers of CA, and $(\text{CA-A})_s$ denotes the electron-acceptor system A ($= s$ LB monolayers

of CA randomly doped with suitable organic π -electron acceptors A). This work was repeated and confirmed by Sugi and co-workers (79), who observed rectification properties, but only if $q \geq 3$, $r \geq 1$, and $s \geq 3$, that is, if there are at least seven monolayers (below that, irreproducible data resulted). In these LB films, the registry and intermolecular approach between D and A dissolved in adjacent CA monolayers cannot be controlled.

A Phase-Change Organic Switch. In 1979 a fast switch was discovered by Potember (80) in CuTCNQ, where TCNQ is 7,7,8,8-tetracyanoquinodimethane. This was due to the thermodynamic metastability (in crystals or amorphous powders) of the violet, low-conductivity ionic state (IS) $\text{Cu}^+ \text{TCNQ}^-$ (c), relative to the yellow, low-conductivity, neutral state (NS) $\text{Cu}^{(0)} \text{TCNQ}^{(0)}$ (c), with, presumably, an intermediate, mixed-valent, higher conductivity state (CS); one could switch between the two states $\text{IS} \leftrightarrow \text{CS}$ either with an applied voltage over a certain threshold value, or by a moderate laser beam, while heat will restore the IS. This is found also in AgTCNQ and in a few other related systems (81). The switching rate is quite fast and can be even used for optical data storage (82), but has not been incorporated in commercial devices. This work has been carried out also with a scanning tunneling microscope (83).

A Molecule-Based Transistor Using Conducting Polymers. Wrighton and co-workers (84, 85) developed a “molecule-based transistor” that uses conducting polymers, either chemically doped polyaniline layers deposited on Au interdigitated electrodes (84) or a 50- to 100-nm “gate” polyaniline polymer between two Au electrodes shadowed with SiO_2 ; this device still has a gain of almost 1000, but also a slow switching rate (10 kHz), limited by ionic conduction rates (85). Stubb and co-workers (86) showed that a single LB monolayer can be used in a molecule-based transistor.

Phase-Change Optical Memories. There are four established technologies for mass-information storage and retrieval (87–89):

1. magnetic memories (MM), disks and tapes, based on ferrite, iron oxide, chromium oxide and pure iron (coated with alumina or silica): These are erasable or write-many, read-many (WMMR) media.
2. Si- and GaAs-based semiconductor computer memories (SM): These can be considered as very-fast write-many, read-many (FWMMR) media.
3. Al pits (melted regions, or crystalline-to-amorphous tran-

sition) on polycarbonate-based laser-readable compact-disk (CD) technology: This is a permanent or write-once, read-many (WORM) medium.

4. magneto-optical media (WMRM)

The present limitations in storage density, access time, and cost of the above four techniques have spurred an extensive search for alternative storage strategies. Alternative methods of storing WORM data on CD-type surfaces depend on phase-change systems (opaque to transparent, etc.) that can use inorganic substrates (e.g., Te) or organic substrates, or systems that depend on local melting and moving aside an organic film [e.g., phthalocyanines (90)]. Organic systems may show a cost advantage in optically addressable nonmagnetic WMRM media.

Highly Conducting Langmuir–Blodgett Films. Barraud (Commissariat à l’Energie Atomique, Saclay) and Kawabata (National Chemical Laboratory for Industry, Tsukuba) have worked on many LB multilayer films that are highly anisotropic in their conductivity; they are insulators in the direction normal to the film plane, but conductors in the plane of the film, with anisotropies of the order of 10^{10} (91–93). This is caused by partial charge transfer in the film plane (e.g., between TCNQ⁰ and TCNQ[−], or between TTF⁰ and TTF⁺, where TTF is tetrathiafulvalene) and by the formation of partially crystalline π -stacks in the plane of the film, very similar to those exhibited in anisotropic quasi-one-dimensional conducting crystals like TTF TCNQ. The only difference is the much higher anisotropy.

Spin Transitions in Langmuir–Blodgett Films. The groups of Barraud and Kahn (University of Paris) have demonstrated hysteretic bistability in an LB film of 200 monolayers of Fe(tris-alkylated-1,10-phenanthroline)₂(isothiacyanate)₂ (94).

Connections to a Unimolecular Electronic Device

Before we review the currently active proposals for truly unimolecular devices, we should discuss ideas for how to “talk” to such single molecules or clusters, that is, how to get signals to and from the macroscopic world of electronics ($>1\text{ }\mu\text{m}$) to the “nanoscopic” world of single molecules (perhaps through an intermediate “mesoscopic” world of sizes of the order of $1\text{ }\mu\text{m}$ – 100 nm).

To address a single molecule electrically, one needs a “molecular wire” (63) (e.g., a polyacetylene strand) or a “molecular antenna” (95) (e.g., the conjugated portion of β -carotene), neither of which can be easily connected to an external potential source, at present. Until the recent advent of the STM (46), one could not connect a single molecule

to an external circuit. Therefore, when the ORP was initiated, in about 1981, to realize the Aviram–Ratner rectifier, one had to content oneself with one-molecule-thick planar assemblies of molecules.

The three techniques that showed promise were as follows: (1) the LB technique (35–41), and the technique of covalently bonding molecules to electrode surfaces, either by (2) silanizing a hydroxyl-coated electrode and then attaching molecules covalently (96), or (3) by silanizing the molecule and attaching it directly by spin-coating by the oleophobic method (97) to a hydroxyl-coated electrode (98). As discussed previously, good monolayer coverage is claimed for methods 2 and 3 (98), but not for method 1 (96).

Macroscopic Connections: Langmuir–Blodgett and Langmuir–Schaefer Films. If one cannot address a single molecule, one can perhaps address a monolayer of identical molecules transferred to a suitable (metal) substrate by the LB (vertical transfer) or LS (horizontal transfer) methods. If the support is electrically conducting and a metal probe is gently lowered atop the LB monolayer or multilayer, then many identical molecules can be addressed electrically, provided that electrical short circuits through defects do not occur. However, LB monolayers are only weakly physisorbed to surfaces, and thus can reorder, recrystallize, or even desorb with time. This difficulty can be circumvented if a photopolymerizable [e.g., diacetylene (99)] group is included in the monolayer-forming molecule and if the molecular geometry is so engineered as to yield topotactic polymerization; this can result in a very robust, yet electroactive, polymer. In some cases, polymers at the air–water interface transfer well onto solid supports.

One should also remember the free-standing bilayer lipid membranes (BLM), pioneered by Mueller (100) and Montal (101). A very delicate and ephemeral BLM is formed when a thin hydrophobic support with a 1- to 10-mm hole is lowered into water and a monolayer is transferred to it on both sides of the support, and also across the hole. The BLM will have the hydrophobic parts of the two monolayers touching across the hole, so that an artificial bilayer membrane similar to that of cell walls is obtained, which is useful for electron-transport studies.

Macroscopic Connections: The Silyl Bridge. An alternate connection strategy, devised by Murray (96) to study the electrochemistry at the electrode surface more closely, consists of derivatizing an oxide-coated metal-electrode surface with trichlorosilyl groups and then reacting this surface with the desired molecule that has a terminal alcohol group; this, however, does not usually give full monolayer coverage on the metal. The reverse strategy, advanced by Sagiv (97), starts with the self-assembling “oleophobic” membranes of Zisman (98) and silanizes

the molecule and attaches it to an oxide and hydroxyl-group-covered metal surface, thereby achieving full monolayer coverage. An interesting variant of Sagiv's technique allows the sequential assembly of well-designed multilayers covalently attached to each other and to a hydroxyl-coated surface (102). Thiols and other S-containing compounds chemisorb well onto Au (103, 104).

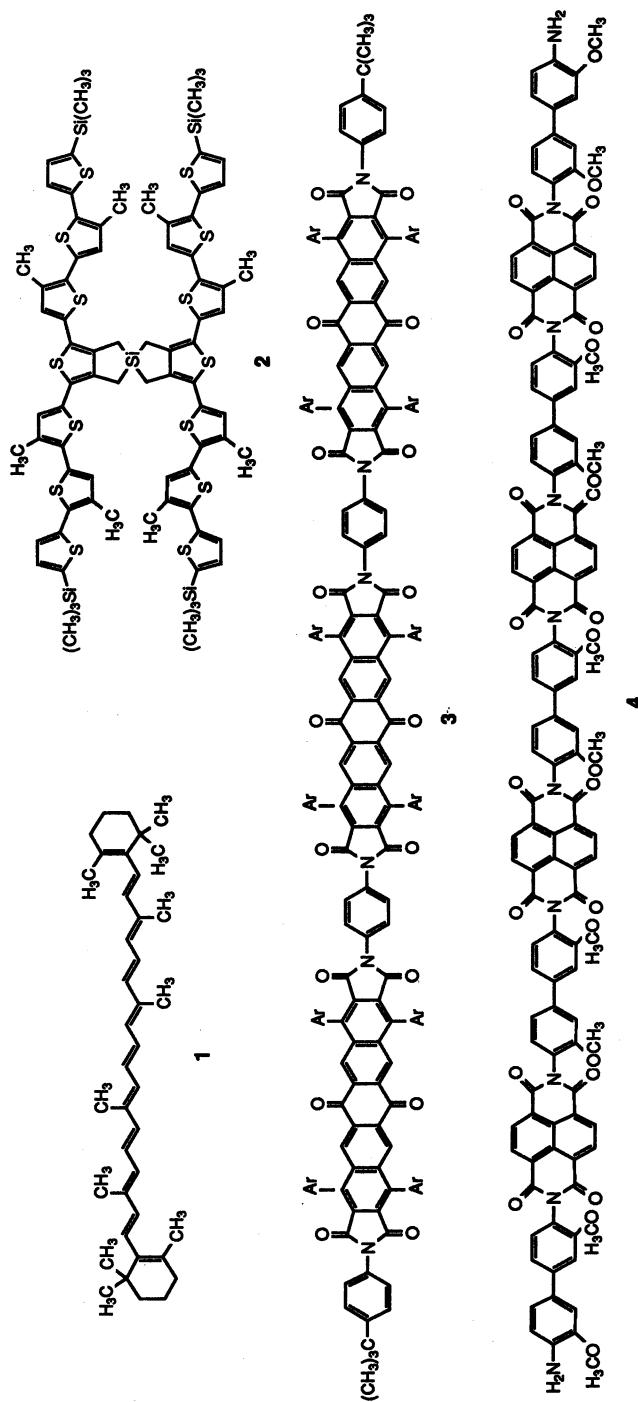
Macroscopic Connections: Cyclodextrins, Calixarenes, and Zeolites. The existence of cavities of precisely controlled size within cyclodextrins and calixarenes allows the inclusion of small electroactive molecules within these cavities and yet provides well-formed macroscopic crystals with the desired inclusions precisely oriented within them (67, 68). Similarly, the cavities inside zeolites have been exploited by Enzel and Bein (69) to produce strands of conducting polymers inside the channels of zeolites (however, the zeolite-conducting polymer adduct is overall insulating). The connections of such matrices to an external circuit have not been addressed so far.

Mesoscopic Connections: Anchoring onto Quantum Dots. By ion-beam lithography "quantum dots" have been produced on Si that are only 100 nm across (but there is hope to make them about 10 nm across) (105). Wrighton has proposed that adjacent quantum dots A and B, coated by different metals, for example, Au and Al, could be bridged by a designed molecular rectifier molecule X -D- σ -A-Y, where the X end will chemisorb on dot A but not on B, whereas the Y end will chemisorb on quantum dot B, but not on A. Then a potential across the quantum dots will enable directed currents through the molecule (Wrighton, M., private communication).

Proposed Nanoscopic Connection: Molecular Wires. The natural sacrificial antioxidant β -carotene (**1**) has been touted as a molecular wire (63) or as a molecular antenna (95) and certainly will provide fast electronic access to single molecules. Such polyenes are, unfortunately, very susceptible to air oxidation (as is doped polyacetylene, the simplest conducting polymer).

Nanoscopic Connection: Spiro-Linked Thiophene Intercircuit Connections. Aviram proposed (64) a spiro-linked polythiophene system to interconnect two mutually perpendicular conducting molecular wires, both of which consist of *n*- or *p*-doped polythiophene. Such a molecule (**2**) has been synthesized (65).

Nanoscopic Insulators: Molecular Lines. Several successive Diels-Alder condensation reactions can yield insulating, yet sturdy, LB film-forming oligomers of controlled length (**3**, **4**) (66).



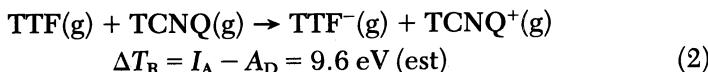
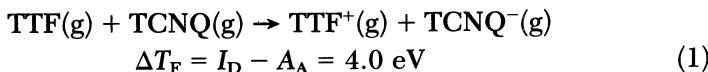
Nanoscopic Connection: Scanning Tunneling Microscopy. The recent advent of STM (46) as an affordable research technique should allow the electronic addressing of a single molecule. If this becomes easily controllable and reproducible, then a real revolution in ME devices should be “just around the corner”. Indeed, an STM has been used to demonstrate tunnel diode behavior (106). However, as experience with STM accumulates, one must learn to beware of false images [“seeing what one wants to believe,” e.g., DNA on graphite (107, 108)], to account for reconstructions of the conducting surface by the tip (109), and to understand the force applied by the atomically sharp tip onto a weakly chemisorbed species like an LB or LS film; this force may burrow the tip rather deeply within the LB monolayer or may create artificial furrows within it (Hansma, P. K., private communication).

Truly Unimolecular Devices

We next consider ideas to achieve unimolecular or zero-dimensional electronic devices.

Proposed D- σ -A Rectifier. The Ansatz of Aviram and Ratner (2–4) starts from the discovery of highly conducting lower dimensional organic charge-transfer (CT) systems based on good one-electron donors (D) such as TTF (5) and good organic one-electron acceptors (A) such as TCNQ (6).

Good donor molecules (i.e., molecules with relatively low gas-phase first-ionization potentials I_D) are, at the same time, poor acceptors (they have low electron affinity A_D); good acceptors (i.e., molecules with a relatively high first-electron affinity A_A) are, at the same time, rather poor donors (have high I_A); thus the gas-phase energy ΔT_F required for charge transfer (both components at infinite separation) is about 4 eV (electronvolt) (eq 1), whereas the energy ΔT_R required for the reverse reaction would need over 9 eV (eq. 2):



Thus, the “Gedankenmolkūl” D- σ -A (7), if assembled between two metal electrodes M_1 and M_2 , as in Figure 2b (discussed as $M_1|\text{D-}\sigma\text{-A}|M_2$ in the section, “The Aviram–Ratner Organic Unimolecular Rectifier”), will exhibit easy electron transfer from M_1 to M_2 because the relatively accessible zwitterionic state $\text{D}^+\text{-}\sigma\text{-A}^-$ is used (while the electron flow from M_1 to M_2 would be inefficient, because the barrier to form the

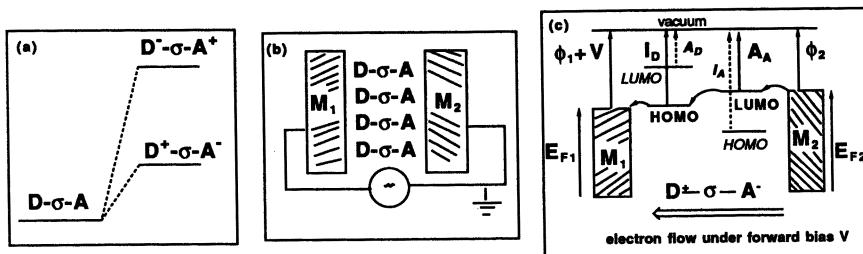
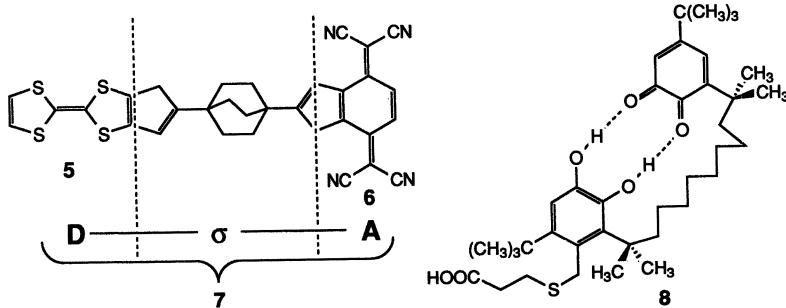
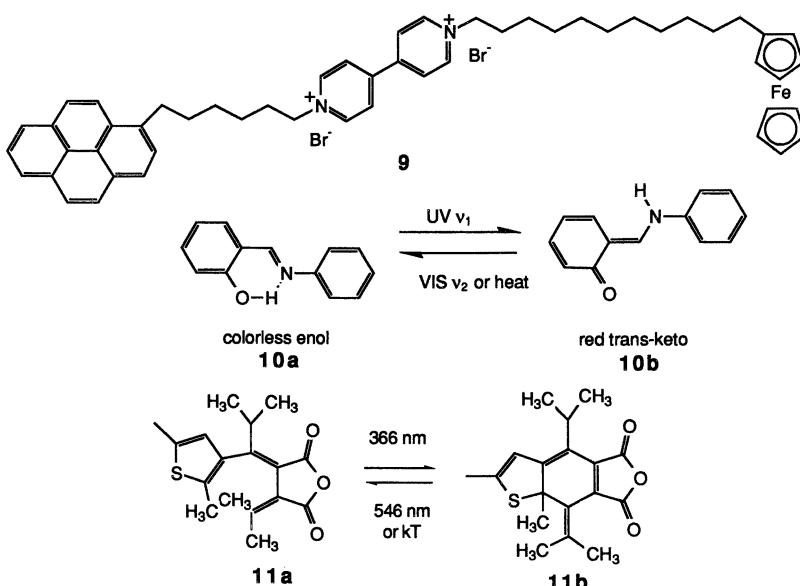


Figure 2. The Aviram–Ratner Ansatz. **a,** Reason for electronic asymmetry: The zwitterion $D^+-\sigma-A^-$ is many electron volts lower in energy than the other zwitterion $D^-\sigma-A^+$. **b,** Connection of an oriented monolayer between two macroscopic metal electrodes M_1 and M_2 ; this is the device $M_1|D-\sigma-A|M_2$, grounded at M_2 . **c,** If, under moderate forward electrical bias applied to the device $M_1|D-\sigma-A|M_2$, the work function ϕ_2 of the grounded macroscopic metal electrode M_2 matches in energy the electron affinity A_A of the lowest unoccupied molecular orbital (LUMO) of the A side of $D-\sigma-A$ (equal distance from the vacuum level to the LUMO of A), and if the work function ϕ_1 , plus the applied voltage V , of metal electrode M_1 matches the ionization potential I_D of the highest unoccupied molecular orbital (HOMO) of the D side of $D-\sigma-A$ (equal distance from the vacuum level to the HOMO of D), then, since I_D is typically larger than A_A , the tunneling through the barrier is assisted only in the direction shown, and rectification of electrical current is achieved. (In italics are shown the HOMO of the acceptor and the LUMO of the donor, and the energies I_A and A_D .)

zwitterion $D^-\sigma-A^+$ would be several eV higher). The Aviram–Ratner device will work if the tunneling of electrons from A to D is assisted “through the bond system” (110) and will fail if the electron transfer between the metal electrodes M_1 and M_2 is predominantly by direct, unassisted, ordinary “through space” tunneling. Molecule 7 was never synthesized, and the idea languished until the ORP started in earnest, as is chronicled later in this chapter.





Proposed H Atom and Proton Transfer Switches. Aviram has also proposed an intramolecular hydrogen atom transfer switch, based on H bonding in ortho-quinone–catechol systems (3, 4); there is intramolecular H-atom transfer in such a system (8) (111, 112). Mitani is working toward a proton transfer switch (60).

Proposed Soliton Switch. The late Forrest L. Carter (61) proposed that soliton motion in polyacetylenes could be harnessed in various switches, gates, and logic circuits. However, apart from the difficulties of synthesizing or addressing such molecules, soliton switches are expected to be relatively slow devices.

Fujihira's Langmuir–Blodgett Photodiode. Fujihira and co-workers (62) have demonstrated that a single LB monolayer can function as a photodiode, probably the first truly unimolecular device. They synthesized a D- σ_1 -A- σ_2 -S molecule (**9**), where D is electron donor, ferrocene; σ_1 is the (CH₂)₁₁ chain; A is the final electron acceptor, viologen; σ_2 is the (CH₂)₆ chain; S is sensitizer, pyrene. This molecule was transferred as an LB monolayer onto a semitransparent Au electrode (with the viologen or A part of molecule closest to Au). The electrode was the side of an electrochemical cell containing a 0.1-M KCl solution

and a Pt counter electrode. Under bias, an electron is transferred from solution to the ferrocene end of the LB film and then to the ground state of the pyrene molecule. Ultraviolet light at 330 nm excited the pyrene radical cation from the ground state to an excited state, from which the electron is transferred to the viologen, thus completing the circuit. A photocurrent of 2 nA at 0.0 V versus the standard calomel electrode (SCE) was observed only whenever the light was turned on (62).

Light-Induced Intramolecular Rearrangements. Sixl (113) suggested using the photochromism of *N*-salicylideneaniline (10), where the enol configuration can be converted to the *trans*-keto conformation by using light of frequency ν_1 , and converted back by either heat or by light of frequency ν_2 . Keto–enol tautomerism is accompanied by an intramolecular rotation. Another light-induced rearrangement in a fulgide (11) has been studied recently (114).

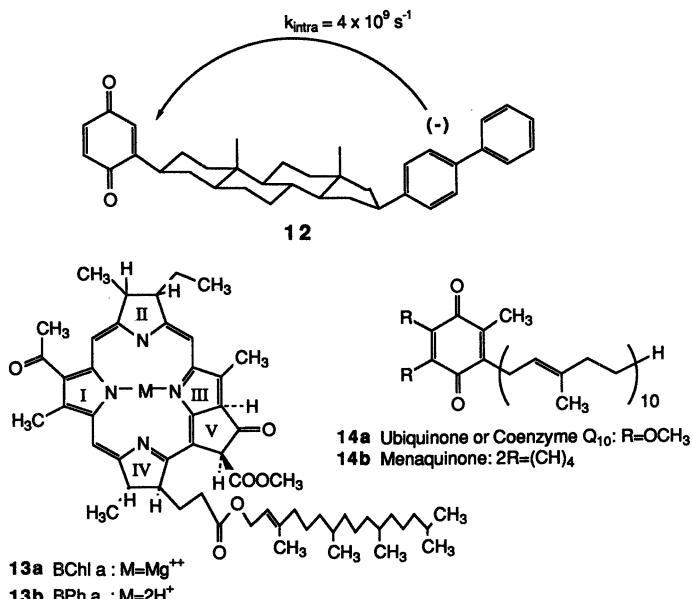
Conductivity Change in Langmuir–Blodgett Films Due to Light-Induced Conformational Change. The late Yasujiro Kawabata and co-workers (115) showed that a light-induced *cis*–*trans* conformational change in azobenzene affects the in-plane electrical conductivity of an LB film.

Potential Conformational Change Systems. The idea of using organic molecules that undergo conformational changes in optical storage devices is widespread. Birge (116) studied the primary step in the photocycle of bacteriorhodopsin (the light-harvesting protein of *Halo-bacterium halobium*), in which the bacteriorhodopsin containing all-*trans* retinal (bR568) can be converted (at 77 K), with two-photon illumination at 540 and 635 nm, into K610 or bathorhodopsin; at lower laser powers, the same two-photon illumination scheme can interrogate which molecules have converted to K610 and which remain in the bR568 state. The K610 state may consist of a *cis*–retinal segment. The harnessing of such *cis*–*trans* isomerizations (also involved in the physiology of the visual pigments) may yield interesting molecular devices.

At room temperature, holographic recording of images can be obtained by whole cell membranes (but not the isolated enzyme) deposited on a glass plate (Hampp, N., private communication).

Other D–σ–A and D–π–A Electron Transfer Molecules

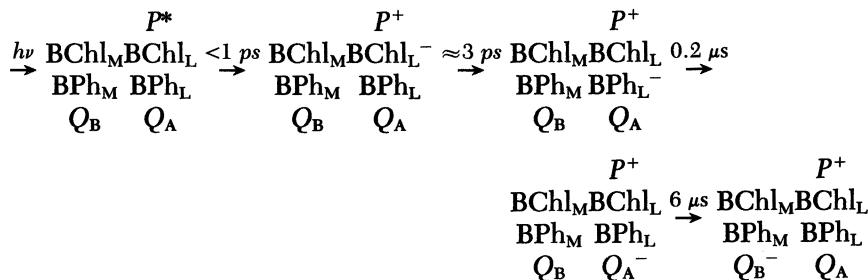
Before discussing the progress toward the Aviram–Ratner D–σ–A unimolecular rectifier, one should mention related molecules of the D–σ–A and D–π–A type, which have been synthesized for studies of intramolecular electron transfer, photosynthesis, organic conductivity, and for new nonlinear optical devices.



Understanding Intramolecular Electron Transfer. Taube pioneered (117) the understanding of intramolecular electron transfer in solution involving binuclear transition metal complexes, both D- σ -A and D- π -A. More recently, efforts have been made to control the electron transfer in solution between D- σ is Creutz-Taube ion [$\text{Ru}(\text{bpy})_3^{2+}$] (bpy is 2,2'-bipyridine), and A is methylviologen (118). Miller, Closs, and co-workers (119, 121) showed that the intramolecular electron transfer rate through molecules D- σ -A such as 12, at first increases steadily with an increasing $I_D - A_A$ (where I_D is the ionization potential of the donor moiety D, A_A is the electron affinity of the acceptor moiety A). Then, if $I_D - A_A$ is increased further, the electron transfer rate decreases, because of an increase in the Franck-Condon reorganization (because the geometries of D^+ and A^- are quite different from the geometry of D and A, respectively) (119–121) [Marcus “inverted region” (122)]. In the experiment, performed in a low-temperature glass, the electron “donor” is really the biphenyl radical anion (which initially captures an electron from a linear accelerator; thus biphenyl radical anion acts as the initial acceptor A'; the ultimate electron acceptor A is varied (A is benzoquinone in 12). Thus the system is really A'- σ -A, instead of D- σ -A, and the intramolecular electron transfer rates correlate with differences in the electron affinities of A' and A or of their

solution electrochemical reduction potentials. An obvious analogy remains between **12** and D- σ -A systems.

Structure of Bacterial Photosynthetic Reaction Center. A dramatic advance in understanding natural photosynthesis was the crystal structure determination of the photosynthetic reaction centers (RC) of *Rhodopseudomonas viridis* (RV) (123) and of *Rhodobacter sphaeroides* (RS) (124). This RC consists of six tetrapyrrole subunits: a dimeric “special pair” (*P*) of bacteriochlorophyll (BChl, 13a) molecules, two “accessory” BChl’s, two bacterio-pheophytins (BPh, 13b), and a quinone acceptor *Q* (ubiquinone, 14a for RV, menaquinone, 14b for RS). A light photon $h\nu$ is absorbed by *P*, exciting it to P^* ; then an electron is transferred by an irreversible CT process from *P* to Q_A within 200 ps and to Q_B after a further 6 μ s (125–130), as follows:



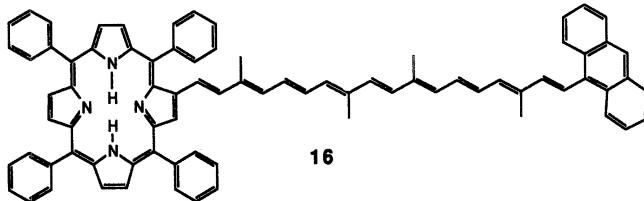
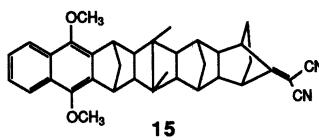
The natural photosynthetic system exhibits a crucial asymmetry: The forward CT converts the initial state D- σ -A into a long-lived charge-separated state $D^+-\sigma-A^-$ (i.e., in nature the back charge transfer (BCT) is much less likely or much slower); thus $D^+-\sigma-A^-$ persists long enough to enable oxidation and reduction chemistry at the physically well-separated D^+ and A^- sites.

Progress toward a Biomimetic D- σ -A Photosynthetic Reaction Center. For an artificial D- σ -A photosynthetic system, the goal is to stabilize the charge-separated state, perhaps by adapting Mother Nature’s trick of using several exoergic electron transfers to the ultimate quinone (BCT becomes statistically unlikely because of the number of “uphill” steps involved). Many model D- σ -A systems have been prepared and studied; a partial list of active research groups and their interesting molecules would include the groups of Bolton (University of Western Ontario) (131), Dervan and Hopfield (California Institute of Technology) (132), Mataga (Osaka University) (133, 134), Mauzerall (Rockefeller University) (135, 136), Staab (Max-Planck-Institute for Medical Research, Heidelberg) (137), Verhoeven (University of Amsterdam) and Padden-Row (University of Sydney) (15) (138, 139), Effenberger and Wolf (University of Stuttgart) (16) (140), Gust and Moore

(Arizona State University) (17) (141, 142), and Wasielewski (Argonne National Laboratory) (18) (95). For 17 the charge-separated final state ($\pi-D^+-\sigma-D'-\sigma-A-\sigma-A'$) has the impressively long lifetime of 55 μs (142).

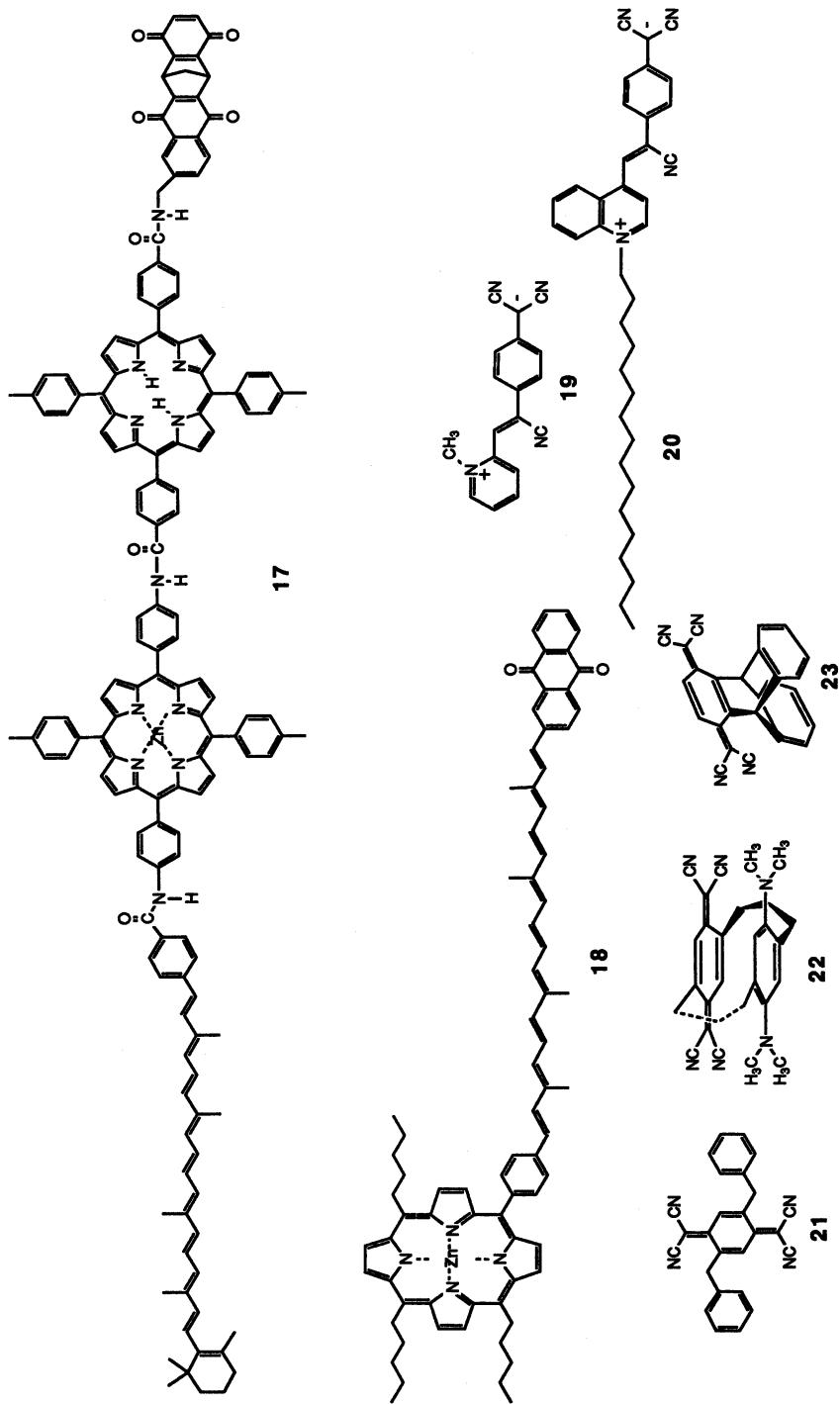
Nonlinear Optical $D-\sigma-A$ and $D-\pi-A$ Molecules. $D-\sigma-A$ and $D-\pi-A$ molecules can also exhibit large second-order nonlinear optical coefficients [β (molecular) or $\chi^{(2)}$ (bulk)]; which become large when the electron-donating group D and the accepting group A are separated by a large distance, because this increases the molecular dipole in both ground and excited states (143). The potential application is for frequency doubling (second-harmonic generation). Powerful and inexpensive primary lasers are not available in the visible and ultraviolet regions of the spectrum, and the output of IR lasers is usually frequency-doubled with expensive inorganic nonlinear optical crystals such as lithium niobate and potassium dihydrogen phosphate (143). An interesting set of zwitterionic molecules, were derived from P3CNQ (19) (144, 145), for example, $C_{16}H_{33}-Q3CNQ$ (20), which has a very high calculated β (146, 147).

Unusual $D-\sigma-A-\sigma-D$ and $D=\sigma=A$ Molecules. Becker et al. (148) (University of the Negev, Beersheba) prepared 21, ($D-\sigma-A-\sigma-D$) where A, which is TCNQ, is linked to two benzyl groups ($D-\sigma$ are weak donors), whereas the group of Staab (149) attempted to make a TTF-TCNQ phane ($D=\sigma=A$) as a potential new organic conductor, but achieved the synthesis of 22 instead. In studies of Mulliken intramolecular CT, Murata's group (150) (Osaka University) synthesized 23 and several methoxy derivatives thereof.



The Aviram–Ratner Organic Unimolecular Rectifier

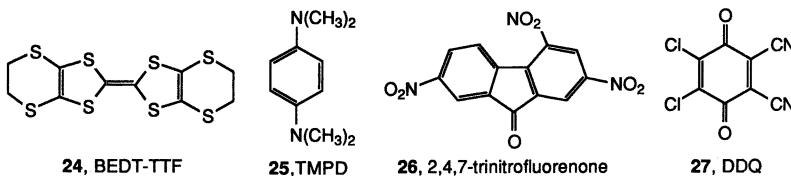
We can now review the progress made toward the synthesis and characterization of the Aviram–Ratner rectifier $M_1|D-\sigma-A|M_2$ (Figure 2b).



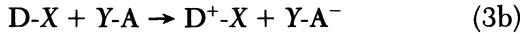
Given that STM was not available when the project started, an initial commitment was made to the LB technique.

Electronic and Synthetic Criteria. Several interlocking criteria must be satisfied for the rational synthesis of suitable D- σ -A systems:

1. I_D for the donor end D must be as small and as close as possible to the work function ϕ of the metal layer M_1 . Typical values are given in Table I and Figure 3. BEDT-TTF, 24, is the strong donor bis-ethylenedithiolene-tetrathiafulvalene, while TMPD, 25, is the strong donor *N,N,N',N'*-tetramethyl-para-phenylenediamine.



2. A_A for the acceptor end A must be as small and as close as possible to the work function ϕ of the metal layer M_2 . Table I and Figure 3 show that requirements 1 and 2 can be met only approximately. DDQ, 27, is the very strong acceptor 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.
3. In a molecule in which the “sigma” bridge σ has already been built, it is extremely difficult to chemically convert a weak donor into a strong donor or to convert a weak acceptor into a strong acceptor. Therefore, one must first synthesize a monosubstituted strong donor (call it D-X) and a monosubstituted strong acceptor (call it Y-A) and then join them by a coupling reaction (eq 3a) that, somehow, avoids the undesirable but likely formation of ionic CT complexes (eq 3b):



4. The molecules must pack efficiently into self-assembling monolayers or bind covalently to a substrate. If the designed D- σ -A molecule does not form PL (17, 26) self-assembling monolayers at the air-water interface, then either long aliphatic “greasy tails” must be added to form a hydrophobic tail or an ionic, hydrophilic “head” should be added to either the D end or the A end. The molecules

Table I. Experimental Ionization Potentials and Electron Affinities for Selected Donors/Acceptors, and Work Functions for Selected Metals

Donor	I ^a	Ref.	Acceptor	A ^a	Ref.	Metal	ϕ (eV)	Ref.
Benzene (W)	9.38	151	p-benzoquinone (W)	1.9	155	Mg	3.66	158
BEDT-TTF (24, M)	7.6	152	2,4,7-trinitrofluorenone (26, M)	2.2	156	Al(111)	4.24	159
TTF (5, S)	6.83	153	TCNQ (6, S)	2.8	157	Au(111)	5.31	162
TMPD (25, S)	6.25	154	DDQ (27, S)	3.13	156	Pt(111)	5.7	161

^a Values are expressed in electron volts; reference numbers in parentheses.

NOTE. I, ionization potentials; A, electron affinities; ϕ, work functions; W, weak; M, medium; S, strong. For other abbreviations, see text.

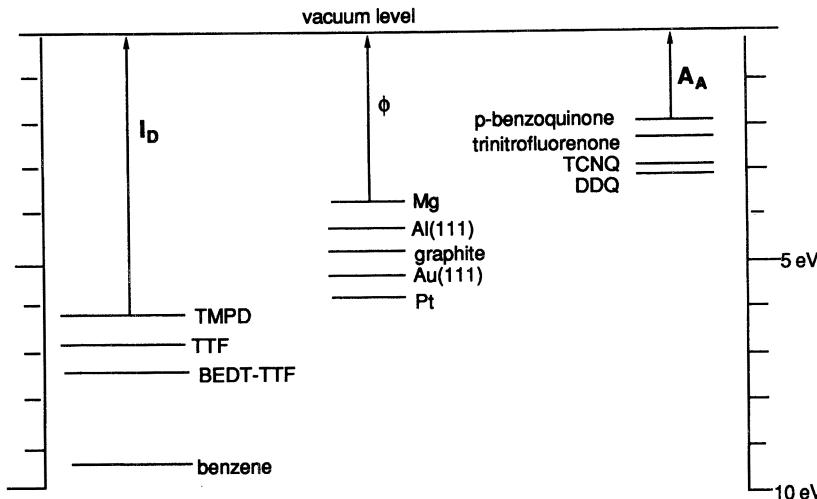


Figure 3. Energy level diagram for donors (I_D), metals (ϕ), and acceptors (A_A).

should be fairly flat, so as to form compact PL films, yet flexible enough, so as to transfer well as LB films (by the vertical or LB dipping method, or by the horizontal or LS method).

5. The electron transfer through the $D-\sigma-A$ molecule and through its hydrophobic or hydrophilic tails must be fast: A molecular device that is small but slow is predicted to be useless. That electron transfer is fast through properly designed molecules (e.g., the photosynthetic reaction center) is well known. The work of Miller, Closs, and co-workers (119–121), reviewed previously, shows that $I_D - A_A$ values must not be too large, to avoid the reduction in electron transfer rates caused by a large Franck–Condon reorganization.
6. The device will have a limited tolerance for high voltages or for heating. A monolayer 2–3-nm thick probably tolerates no more than 1-V external bias across it before dielectric breakdown should occur (2–4, 7)

Practical Criteria for Good Donors and Acceptors. In practice, ionization potentials for all-organic donors range from 6.25 eV for a “strong” donor like TMPD (25) to 9.38 eV for a “weak” donor such as benzene; electron affinities have a much more limited range, from

1.9 eV for a relatively weak acceptor (*p*-benzoquinone) to 3.2 eV for the strongest acceptor (DDQ, 27). The match with metal work functions is not optimal. A long time ago, Matsen (162) and Hush and Pople (163) noted that the ionization potentials (electron affinities) of condensed aromatic hydrocarbons decrease (increase) with increasing molar mass, to meet “at infinity” the work function of graphite, which can be considered as an “infinite” hermaphroditic two-dimensional ideal donor and acceptor: $I_D = A_A = \phi = 4.40$ (164), 4.45 (165), or 4.62 eV (166).

For the Aviram–Ratner unimolecular rectifier, one needs $\Delta T_F = I_D - A_A > 0$ to ensure that “down-hill” through-bond assisted inelastic electron tunneling from A^- to D^+ ; this condition is trivially realized. From Table I, one sees $\Delta T_F = 3.1$ eV (for TMPD and DDQ), 4.0 eV (for TTF, 5 and TCNQ, 6), 5.2 eV (for pyrene and 2,4,7-trinitrofluorenone, 26), 7.6 eV (for the “weak” electron donors and acceptors benzene and *p*-benzoquinone). However, if ΔT_F is too large, then the Franck–Condon factor becomes too small (or the molecular reorganization energy becomes too large), and through-bond electron transfer rates will become too slow. In fact, the work of Miller, Closs, and co-workers (119–121) suggests that maximum electron transfer rates (faster than 10^9 /s) through androstane σ -skeletons are obtained when $\Delta T_F \approx 1.25$ eV (estimated from solution half-wave reduction potentials) and will become slow if ΔT_F approaches either 0 or 2.5 eV. Confronted by the large size of ΔT_F Aviram and Ratner argued that, by formation of mixed-valent stacks of TTF donors and TCNQ acceptors in the LB film, the energy barriers to ionization and electron capture would be reduced in the film state.

The energy levels shown in Figure 3 suggest that a good combination for the device $M_1|D-\sigma-A|M_2$ is $M_1=Pt$, $D=TMPD$, $A=DDQ$, $M_2=($ either Mg or Al): Mg should allow the zwitterion $D^+-\sigma-A^-$ to form at about 0.5-V bias and Al at 1-V bias. As a rough guide for the synthetic chemist, one would prefer $I_D < 7$ eV and $A_A > 2.5$ eV. Because gas-phase ionization potentials, and particularly gas-phase electron affinities are not easily accessible to the organic chemist, a convenient, if more approximate, measure of electronic activity may be the voltammetric half-wave oxidation or reduction potential $E_{1/2}$. Suitable target values are discussed in the section “Cyclic Voltammetry”.

One may also define an asymmetry parameter ΔE :

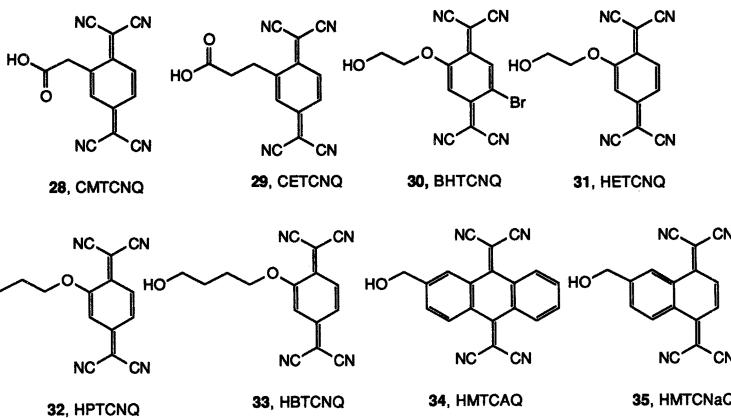
$$\Delta E = \Delta T_F - \Delta T_R = (I_D - A_A) - (I_A - A_D) = (I_D + A_D) - (I_A + A_A) \quad (4)$$

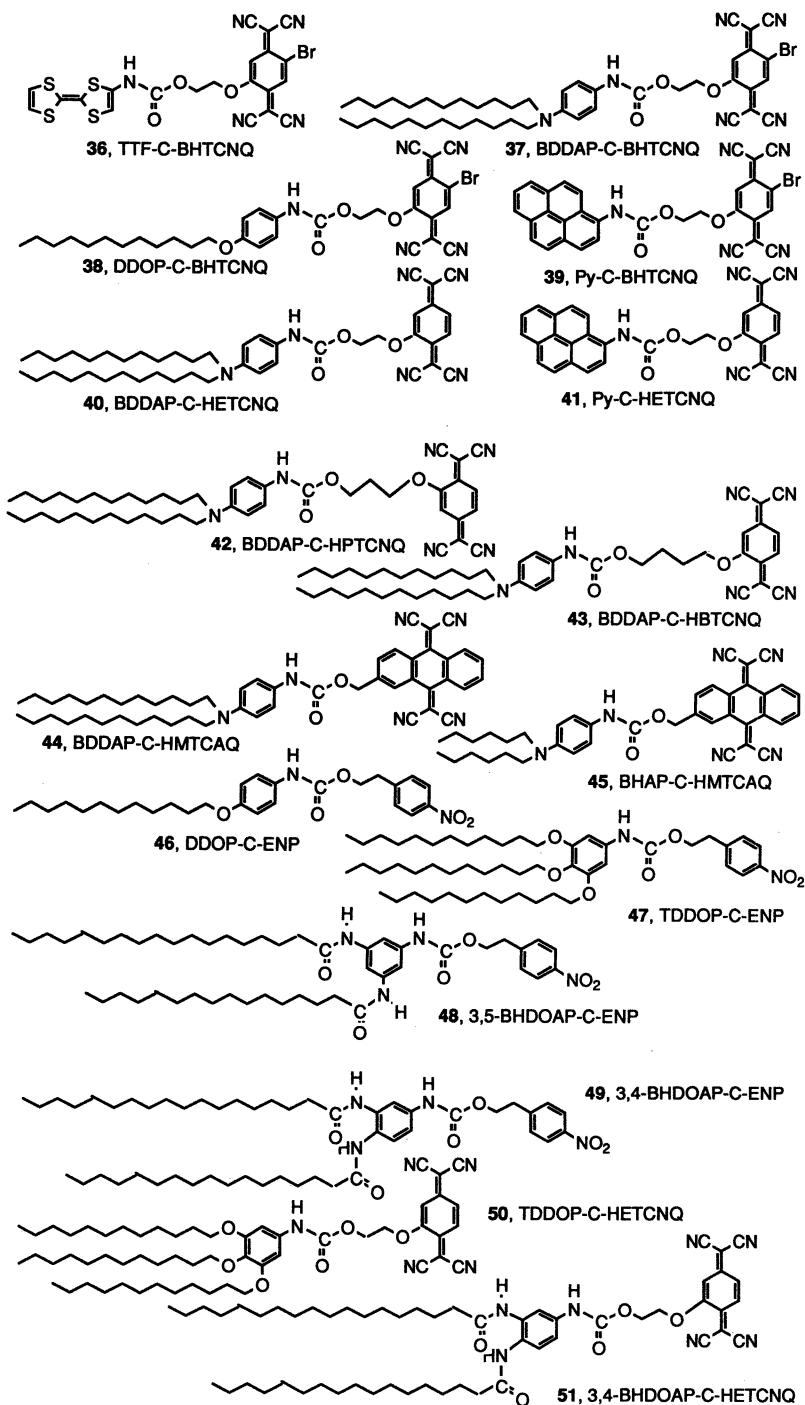
which should help to quantify the electronic asymmetry required in a $D-\sigma-A$ molecule.

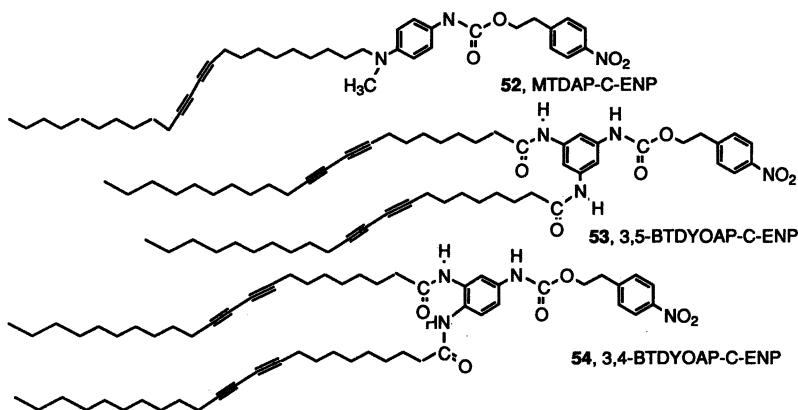
Synthesis. Monofunctionalized TTF compounds, such as TTF-Li, TTFCH₂OH, and TTF-COOH, were pioneered by Green (167). Hertler (168) had coupled a bifunctional TTF to a bifunctional TCNQ alcohol

via the urethane, or carbamate coupling reaction, yielding a semiconducting copolymer ($-\sigma$ -TTF- σ -TCNQ-)_x and had also prepared a monofunctional alcohol (168).

The monofunctional TCNQ compounds carboxymethylene TCNQ (CMTCNQ, 28) and carboxyethylene TCNQ (CETCNQ, 29) were prepared, but would not couple with TTF-CH₂OH (5). The monofunctional TCNQ alcohol 2-bromo-5-hydroxyethoxy TCNQ (BHTCNQ, 30) (168) was found to couple to TTF isocyanate (TTF-NCO, generated from TTF-Li), to yield a TTF-carbamate-BHTCNQ (TTF-C-BHTCNQ) (6-8), and to carboxy TTF (TTF-COOH), to yield a TTF-ester-BHTCNQ (TTF-E-BHTCNQ) (8). Both of these products were obtained in low yield, and in two phases, one of which was ionic, the other neutral. Then the attention was turned to carbamates obtained by coupling BHTCNQ to phenyl, 1-pyrenyl, and *N,N*-dialkyl-aminophenyl isocyanates (9-33) (the latter can be thought of as modifications of TMPD). The synthesis of BHTCNQ (168, 169) contained a very inefficient, low-yield step; a new, monofunctionalized acceptor, prepared in higher yield, was hydroxyethoxyTCNQ (HETCNQ, 31) (19). Two other acceptors, hydroxypropoxy TCNQ (HPTCNQ, 32) and hydroxybutoxyTCNQ (HBTCNQ, 33) were also prepared by similar routes (170). An easily synthesized acceptor was 2-hydroxymethyl-11,11,12,12-tetracyano-9,10-anthraquinodimethane (HMTCAQ, 34), but both HMTCAQ and its underivatized parent molecule (171) are both weak two-electron acceptors: The *peri* hydrogens force them into a butterfly-shaped configuration. A final acceptor was 2-hydroxymethyl-9,10-tetracyano-5,8-naphthoquinodimethane (HMTCNaQ, 35), whose crystal structure has been determined (34); however, it decomposed instead of coupling with phenyl, 4-(dimethylamino)phenyl or 1-pyrenyl isocyanates (34).







Carbamates and esters were thus obtained with BHTCNQ, HETCNQ, HPTCNQ, HBTCNQ, and HMTCAQ as acceptors. The various D- σ -A molecules that form LB films were the carbamates 36–54. Of these, 46–54 were prepared to incorporate D- σ -A molecules into polymerizable diacetylenes, which may yield promising nonlinear optical materials, primarily for frequency doubling: 46–51 were “trial molecules” without diacetylenes, mostly with the weak ethoxynitrophenyl (ENP) acceptor group. To explain the acronyms used for structures 42–54, BDDAP-C-BHTCNQ is the *N,N*-bis-dodecyl-*p*-aminophenyl carbamate of 2-bromo-5-hydroxyethoxyTCNQ, whereas MTDAP-C-ENP is the *N*-methyl-*N*-triseikosi-10,12-diyl-*p*-aminophenyl carbamate of ethoxy-*p*-nitrobenzene (not the world’s most systematic name!).

One can speculate why carbamate coupling reactions failed with CMTCNQ, CETCNQ, and HETCNQ, but succeeded (eq 3a) with BHTCNQ, HETCNQ, HPTCNQ, HBTCNQ, and HMTCAQ. The planned σ bridge length is the number of C, O, or N atoms between D and A ends: 4, CMTCNQ and HMTCAQ; 5, CETCNQ; 6, BHTCNQ and HETCNQ; 7, HPTCNQ; and 8, HBTCNQ. Because the carbonyl group provides partial conjugation within the bridge, up to two atoms from the donor, one can surmise that, at least for the strong acceptor TCNQ, a four to five atom bridge length is too short for a coupling reaction to occur. Naturally, if the bridge is too long (say, >8 atoms) and flexible, then conformational freedom may allow the D and A ends to move to within intramolecular overlap, thereby creating a horseshoe-shaped molecule with internal CT, which may not function as a rectifier.

Cyclic Voltammetry. Donors, acceptors, and several D- σ -A molecules were characterized by cyclic voltammetry (CV). Table II summarizes the results and also contains literature data about related donors and acceptors 55–70, which should be useful for future D- σ -A syntheses. Figure 4 shows the CV for BDDAP-C-HETCNQ, 40.

Table II. Solution Cyclic Voltammetric Half-Wave Potentials, (V vs. SCE), Gas-Phase Vertical Ionization Potentials, and Electron Affinities for Donors, Acceptors, and D- σ -A Molecules

Molecule	Note	Oxid. (1) $D \rightarrow D^+$	Oxid. (2) $D^+ \rightarrow D^{2+}$	Red. (1) $A^- \rightarrow A^-$	Red. (2) $A^- \rightarrow A^{2-}$	Oxid. $D \rightarrow D^+$	Red. $A \rightarrow A^-$	
		$E_{1/2}$ (V)	$E_{1/2}$ (V)	$E_{1/2}$ (V)	$E_{1/2}$ (V)	I (eV)	A (eV)	
						Ref.	Ref.	
Donors								
TMPD (25)	a	0.10	0.66	—	—	14	6.25	—
TTF (5)	a	0.01	0.35	0.75	—	153	—	154
	a	0.37	0.75	—	—	172	6.83	—
	a	—	—	—	—	152	6.70	—
BEDT-TTF (24)	a	0.54	0.96	—	—	172	6.92	—
	a	0.54	0.85	—	—	152	—	174
Pyrene (55)	a	1.16	—	—	—	175	7.41	—
Anthracene (56)	a	1.09	—	—	—	175	7.55	—
Benzene	a	2.30	—	—	—	175	9.38	—
TTFCOCl (57)	a	0.602	0.936	—	—	179	—	—
DMAP-C ₆ Me (58)	a	0.55	—	—	—	14	—	—
BDDABA (62)	b	1.09i	—	—	—	180	—	—
Acceptors								
TCNQ (6)	a	—	—	0.127	-0.291	181	—	157
	a	—	—	0.17	-0.37	182	—	—
	a	—	—	0.19	-0.35	183	—	—
	c	—	—	0.151	-0.403	32	—	—
	d	—	—	0.54	-0.13	186	—	—
	d	—	—	0.53	0.02	182	—	—
TCNOF ₄ (63)	e	—	—	0.51	-0.30	185	—	—
DDQ (27)	a	—	—	0.54	-0.13	186	—	—
DCNQI (64)	d	—	—	-0.481	-1.030	185	—	—
p-Benzoquinone (65a)	a	—	—	—	—	1.91	1.95	155
9,10-Anthraquinone (66)	a	1.21	—	-0.98	-1.50	187	1.98	177
	a	—	—	—	—	188	1.59	155
Chloranil (65b)	a	—	—	+0.01	-0.71	189	2.76	177
Bromanil (65c)	a	—	—	0.00	-0.72	189	—	—
Fluoranil (65d)	a	—	—	-0.04	-0.82	189	2.92	177
2,4,7-Trinitrofluorenone (26)	a	—	—	-0.42	-0.67	190	2.2	156
C ₆₀	d	—	—	-0.18	-0.58, -1.07	191	2.6	192
							2.8	193

TCNE (67)	<i>a</i>	—	—	0.152	—0.568	181	2.3	194
CMTCNQ (28)	<i>a</i>	—	—	0.236	-0.267	32	2.9	195
CETCNQ (29)	<i>a</i>	—	—	0.222	-0.275	32	3.17	196
BHTCNQ (30)	<i>a</i>	—	—	0.305	-0.170	9		
HETCNQ (31)	<i>a</i>	—	—	0.107	-0.398	19		
HMTCAQ (34)	<i>c</i>	—	—	0.101	-0.400	32		
TCAQ (68)	<i>a</i>	—	—	—	-0.333	11		
HMTCNaQ (35)	<i>c</i>	—	—	—	-0.334	32		
TCNaQ (69)	<i>g</i>	—	—	—	-0.390	171		
D- σ -A molecules								
TTF-C-BHTCNQ (36)	<i>a</i>	0.75i	0.99i	0.298	—	179		
DDOP-C-BHTCNQ (38)	<i>h</i>	1.21	—	0.25	-0.07	9		
BDDAP-C-HETCNQ (40)	<i>b</i>	0.97i	1.41	-0.08	-0.20i	30		
Py-C-HETCNQ (41)	<i>b</i>	1.01	1.15	0.08	-0.35	30		
BHAP-C-HMTCAQ (45)	<i>b</i>	0.60	—	—	-0.36	30		
TDDOP-C-HETCNQ (50)	<i>b</i>	0.99i	—	0.07	-0.47	26		
DDOP-C-ENP (46)	<i>b</i>	1.39	—	-1.13	—	26		
BDDOP-C-ENP (61)	<i>b</i>	1.66i	—	-1.09	—	26		
TDDOP-C-ENP (47)	<i>b</i>	1.14i	—	-1.15	—	26		
MTDAP-C-ENP (52)	<i>b</i>	0.54	—	-1.06	—	30		

^a Solvent: CH₃CN. Reference electrode: SCE.

^b Solvent: CH₂ClCH₂Cl. Reference electrode: Ag|AgCl. An offset correction of 0.15 V (26) has been added to the measured values to convert them to V vs. SCE.

^c Solvent: CH₃CN. Reference electrode: Ag|AgNO₃. An offset correction of 0.291 V [see HETCNQ (32)] has been added to the measured values to convert them to V vs. SCE.

^d Solvent: CH₂Cl₂. Reference electrode: Ag|AgCl. An offset correction of 0.15 V (26) has been added to convert them to V vs. SCE.

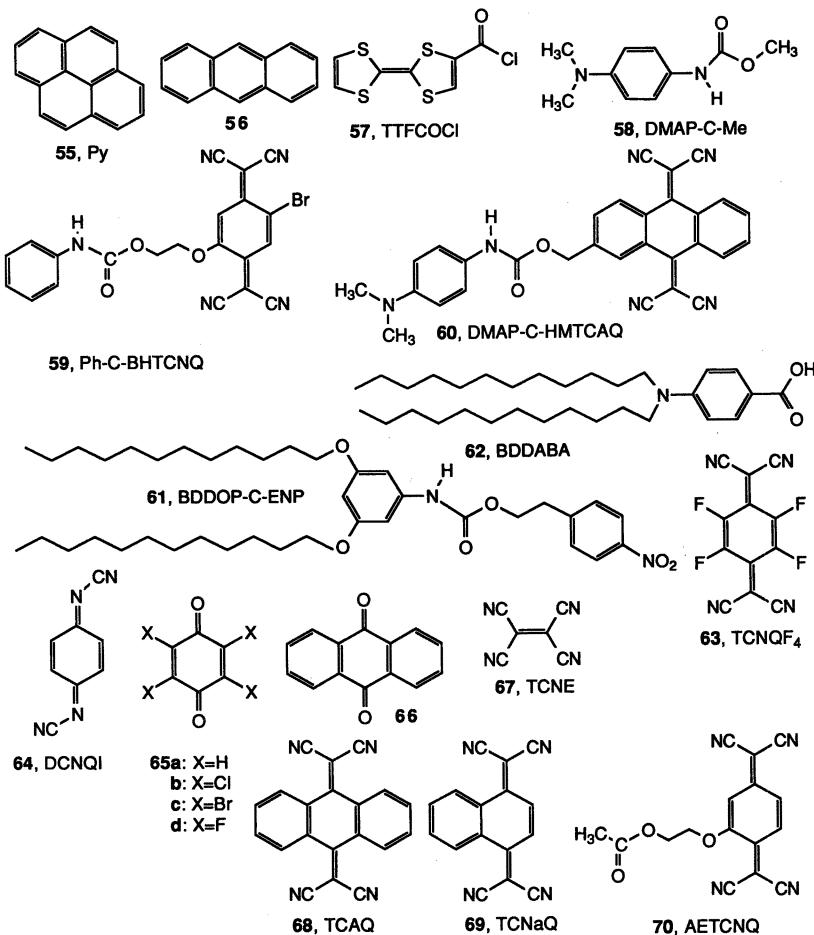
^e Solvent: BuCN. Reference electrode: SCE.

^f Similar to A_A(TCNQ) (160), because $E_{1/2}$ (DCNQI) $\approx E_{1/2}$ (TCNQ) (189).

^g Solvent: CH₂ClCH₂Cl. Reference electrode: Ag|AgNO₃. An offset correction of 0.320 V (9) has been added to the measured values to convert them to V vs. SCE.

^h Solvent: BuCN. Reference electrode: Ag|AgNO₃. An offset correction of 0.320 V (9) has been added to the measured values to convert them to V vs. SCE.

NOTE: $E_{1/2}$, half-wave potentials; V , volts; SCE, standard calomel electrode; I , ionization potentials; A , electron affinities; D, donor; A, acceptor; Oxid., oxidation; Red., reduction; i, irreversible;



It is quite clear from Table II that the solution half-wave potentials ($E_{1/2}$) of the D- σ -A molecules reflect well the reducing and oxidizing properties of the D and A ends, respectively; that is, the carbamate linkages are, in fact, reasonable σ -bridges, and the donor and acceptor functions have been preserved, as planned.

For future work, it may be useful to rephrase the requirements for donors and acceptors in D- σ -A rectifier molecules in terms of approximate limits on solution $E_{1/2}$ potentials, because most organic chemists are unfamiliar with work functions, gas-phase ionization potentials, and gas-phase electron affinities. Several correlations between gas-phase I_D and solution $E_{1/2}$ exist (197–200), and one between A_A and $E_{1/2}$ (156). Naturally, these are only approximate correlations; they do not include the dependence of $E_{1/2}$ on solvent or on the varying size of the solvent cage around molecules of different shapes (152, 201).

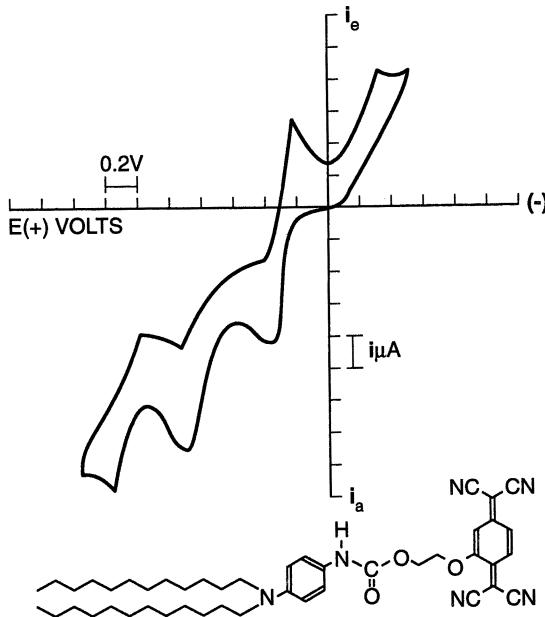


Figure 4. Cyclic voltammogram of BDDAP-C-HETCNQ, 40. (After reference 30).

Using the $E_{1/2}$ values in CH_3CN solution, relative to the standard calomel electrode (SCE), for the donors in Table II a satisfactory approximate correlation (to within ± 0.2 V) is (197) as follows:

$$E_{1/2} = 0.89I_D - 5.70$$

whereas for the strong acceptors DDQ, TCNQ, chloranil, *p*-benzoquinone, and 9,10-anthraquinone an acceptable correlation (to within ± 0.2 V) is

$$E_{1/2} = A_A - 2.62$$

Finally, the criteria for a “good” donor ($I_D < 7$ eV: TMPD, TTF, BEDT-TTF) and a “good” acceptor, ($A_A > 2.5$ eV: TCNQ, TCNQF_4 , DCNQI, chloranil, bromanil, fluoranil, and maybe TCNE or C_{60}), proposed in the section, “Practical Criteria for Good Donors and Acceptors,” become $E_{1/2} < 0.50$ V versus SCE for the donor D and $E_{1/2} > -0.12$ V versus SCE for the acceptor A.

Pockels–Langmuir and Langmuir–Blodgett Films. Table III displays an updated catalog of molecules (13–22) prepared by the ORP, which form PL monolayers at the air–water interface and which transfer

Table III. Pressure-Area Isotherm Data for Pockels-Langmuir Films

Molecule	No.	Type	T/K	Π_c (mN/m)	A_c (\AA^2)	Ref.
TTF-C-BHTCNQ	36	Strong D	292	12.7	134 ± 50	7
		Strong A				
DDOP-C-BHTCNQ	38	Weak D	292	20.2	50 ± 1	9
		Strong A				
BDDAP-C-BHTCNQ	37	Medium D	293	47.3	57 ± 1	17
		Strong A				
Py-C-BHTCNQ	39	Medium D	283	28.2	53 ± 1	9
		Strong A				
BDDAP-C-HETCNQ	40	Medium D	293	40.0	44 ± 1	30
		Strong A				
Py-C HETCNQ	41	Medium D	293	46	—	30
		Strong A				
BDDAP-C-HMTCAQ	44	Medium D	293	22.3	58 ± 1	17
		Weak A				
BHAP-C-HMTCAQ	45	Medium D	293	35.8	42 ± 1	18
		Weak A				
DDOP-C-ENP ^a	46	Weak D	278	23.7	38 ± 1	26
		Weak A				
TDDOP-C-ENP ^a	47	Weak D	278	34.0	76 ± 1	26
		Weak A				
TDDOP-C-HETCNQ ^a	50	Weak D	283	47.5	54 ± 1	26
		Strong A				
3,5-BHDOAP-C-ENP	48	Weak D	299	49.6	39 ± 2	204
		Weak A				
3,4-BHDOAP-C-ENP	49	Weak D	300	54.5	35.8 ± 0.5	31
		Weak A				
3,4-BHDOAP-C-HETCNQ	51	Weak D	300	55.2	51 ± 2	31
		Strong A				
MTDAP-C-ENP ^a	52	Weak D	278	16.5	63 ± 1	25
		Weak A				
3,5-BTDYOAP-C-ENP	53	Weak D	298	18.7	58 ± 2	31
		Weak A				
3,4-BTDYOAP-C-ENP	54	Weak D	300	49.4	50 ± 1	31
		Weak A				

NOTE Π_c and A_c , the pressure and molecular area, respectively, at the collapse point.

^a The film makes Z-type Langmuir-Blodgett multilayers (substrate at 22 °C, film at 5 °C).

well onto Al or glass or other slides as LB monolayers. TTF-C-BHTCNQ, 36, was difficult to purify; the “neutral” form seemed to deposit “pancake-style” onto the water, and synthetic difficulties forced its abandonment. The strongest films (highest collapse pressure and most vertical pressure-area isotherm) were obtained with BDDAP-C-BHTCNQ, 37 (Figure 5).

The acceptor HMTCAQ used in 44 and 45 was easy to prepare (11), but is well-known to be a weak two-electron acceptor, with a highly nonplanar geometry (24). For D-σ-A systems where A is HMTCAQ, PL films were obtained when the alkyl substituent was bis-hexyl (44) or

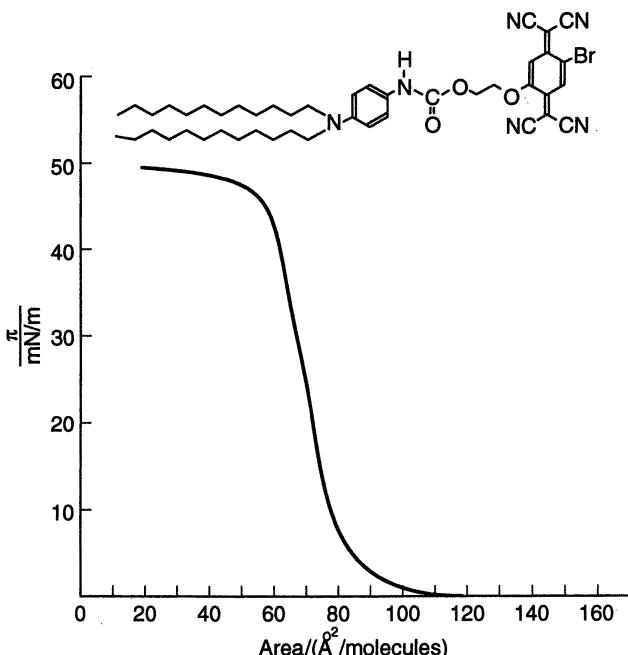


Figure 5. Pressure-area isotherm of BDDAP-C-BHTCNQ, 37, at 293 K.
(Reproduced with permission from reference 16. Copyright 1988.)

bis-dodecyl (45), but not bis-methyl (60): For 60 crystals were obtained instead, whose structure is discussed below.

Molecules 46–51 are model systems for a related project that aims to incorporate D– σ -A systems into LB-film-forming diacetylenes, which may be polymerized *in situ* on the film balance, for the purpose of preparing new systems with promise as nonlinear optical devices. Interestingly, 46, 47, 50, and 52 form Z-type multilayers on a glass substrate (the film subphase is held at 5 °C, but the slide is at room temperature).

Crystal Structures of Model Donor, Acceptor, and D– σ -A Molecules. A few crystal structures have been solved: for the donor DMAP-C-Me, 58 (13) (Figure 6), for the acceptor BHTCNQ, 30 (15) (Figure 7), and for the methyl ester (AETCNQ, 70) of the acceptor HETCNQ, 31 (16) (Figure 8), and for HMTCNaQ, 35 (34). Here ACETCNQ is the acronym for acetylthoxy TCNQ. The small difference in conformation between AETCNQ and BHTCNQ can be attributed to crystal packing forces, rather than to intramolecular effects. Amphiphilic molecules that form LB films will not usually crystallize, because of the usual aliphatic “tails” added to them. The structures of two D– σ -A molecules, which do not form PL or LB films, were solved: Ph-C-

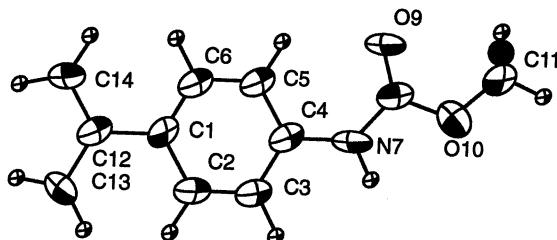


Figure 6. ORTEP-II plot of the crystalline structure of DMAP-C-Me, 58. Space group $Pbca$ (#61), $a = 13.926$, $b = 9.999$, $c = 14.854 \text{ \AA}$, $Z = 8$, $R = 5.9\%$ for 786 reflections. (Reproduced with permission from reference 13. Copyright 1988.)

BHTCNQ, 59 (8) (Figure 9) and DMAP-C-HMTCAQ, 60 (24) (Figure 10). Both structures show an extended carbamate linkage; in Ph-C-BHTCNQ, the dihedral angle between the phenyl ring and the six-membered central ring of BHTCNQ is only 8° (8). This gives hope that in LB films of related D- σ -A molecules the carbamate linkage will also be extended.

Molecular Orbital Calculations. As reported previously (22) semiempirical molecular orbital (MO) calculations, using the MNDO

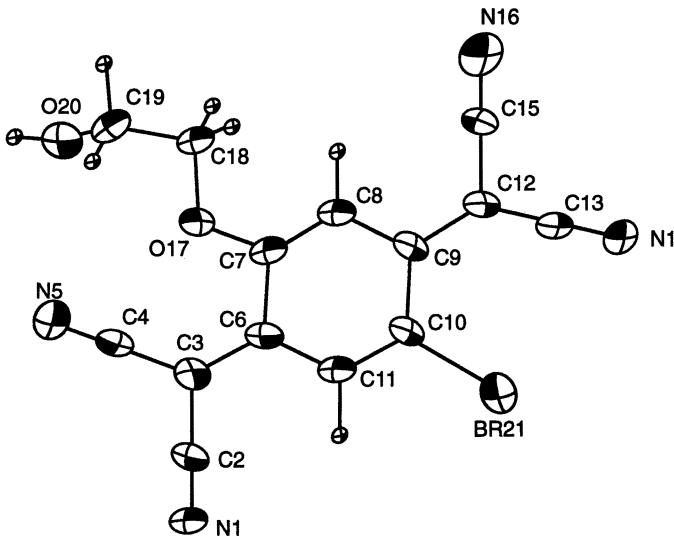


Figure 7. ORTEP-II plot of BHTCNQ, 30. Space group $P2_1/n$ (#14), $a = 9.258 \text{ \AA}$, $b = 13.618 \text{ \AA}$, $c = 10.947 \text{ \AA}$, $\beta = 92.14^\circ$, $Z = 4$, $R = 3.9\%$ for 1395 reflections. (Reproduced with permission from reference 15. Copyright 1988.)

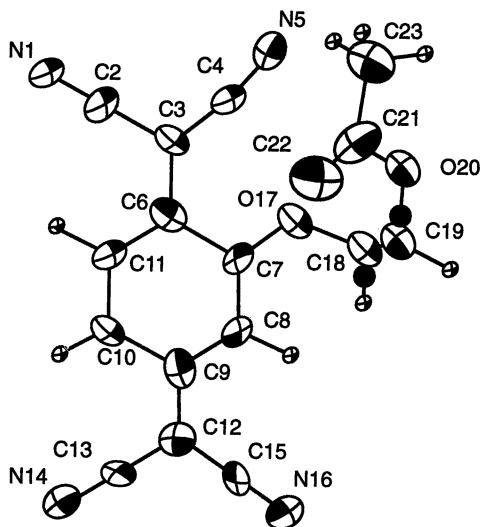


Figure 8. ORTEP-II plot of AETCNQ, 70. Space group $P\bar{1}$ (#2), $a = 7.165 \text{ \AA}$, $b = 9.058 \text{ \AA}$, $c = 13.244 \text{ \AA}$, $\alpha = 70.06^\circ$, $\beta = 87.14^\circ$, $\gamma = 68.22^\circ$, $Z = 2$, $R = 3.4\%$ for 1143 reflections. (Reproduced with permission from reference 16. Copyright 1988.)

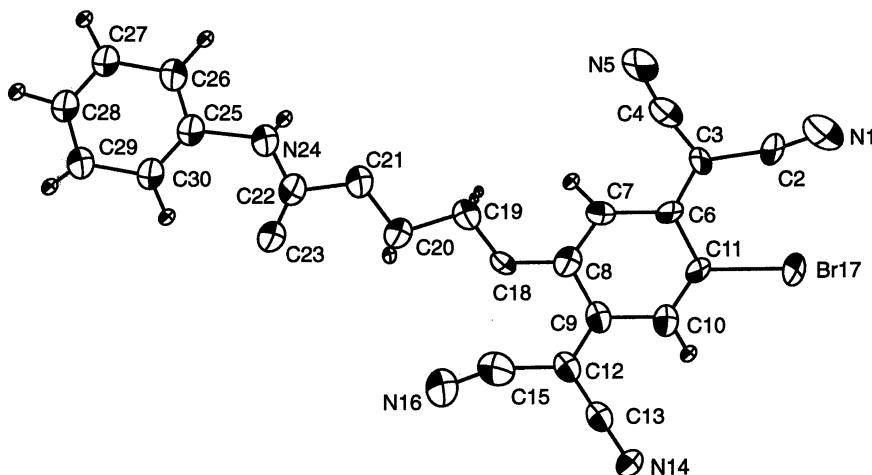


Figure 9. ORTEP-II plot of the crystalline structure of Ph-C-BHTCNQ, 59. Space group $P2_1/n$ (#14), $a = 8.310 \text{ \AA}$, $b = 9.278 \text{ \AA}$, $c = 25.383 \text{ \AA}$, $\beta = 96.15^\circ$, $Z = 4$, $R = 7.9\%$ for 2229 reflections. (Reproduced with permission from reference 8. Copyright 1984.)

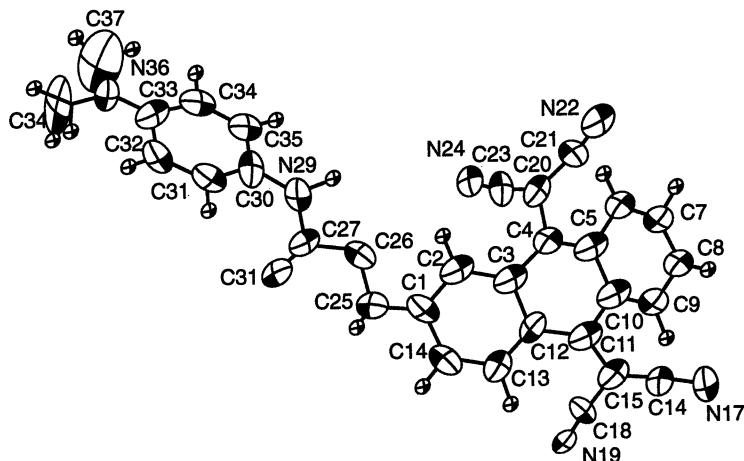


Figure 10. ORTEP-II plot of the crystalline structure of DMAP-C-HMTCAQ, 60. Space group P-1 (#2), $a = 8.748 \text{ \AA}$, $b = 10.989 \text{ \AA}$, $c = 13.541 \text{ \AA}$, $\alpha = 90.67^\circ$, $\beta = 99.15^\circ$, $\gamma = 98.62^\circ$, $Z = 2$, $R = 12.7\%$ for 1839 reflections. (Reproduced with permission from reference 24. Copyright 1989.)

(moderate neglect of differential overlap) algorithm, with full geometry optimization, in computer program MOPAC, have been performed on D- σ -A molecules, to predict their geometry, and also their HOMO and LUMO energies. The Br atom in BHTCNQ was replaced by F for simplicity of calculation. The structures, as drawn by computer program ORTEP-II using typical van der Waals atomic radii (1.2 Å for H, 1.7 Å for C, 1.5 Å for O, 1.35 Å for F, and 1.65 Å for S) are shown in Figures

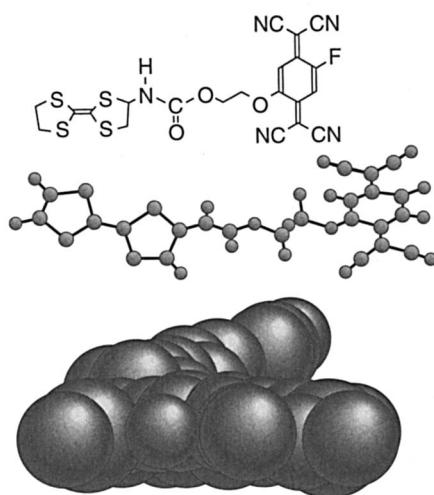


Figure 11. Structure (top), MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) for TTF-C-FHTCNQ, a variant of TTF-C-BHTCNQ, 36; $I_D = 8.197 \text{ eV}$, $A_A = 2.975 \text{ eV}$, $I_A = 9.581 \text{ eV}$, $A_D = 0.134 \text{ eV}$, $\Delta T_F = I_D - A_A = 5.222 \text{ eV}$, $\Delta T_R = I_A - A_D = 9.447 \text{ eV}$, $\Delta E = \Delta T_F - \Delta T_R = 4.225 \text{ eV}$. (Reproduced with permission from reference 22. Copyright 1988.)

11–15 (the van der Waals shape is viewed from the A end of the molecule). Also given are the HOMO ($-I_D$) and LUMO ($-A_A$) energies, and also the differences $I_D - A_A$ and $I_A - A_D$ discussed in equations 1, 2, and 4.

Overall, the MNDO structures are extended, as expected, and as favored by the MNDO parametrization, but there are a few small surprises: (1) whereas the data of Table III suggest that in a PL film Py-C-BHTCNQ is a relatively flat molecule, Figure 14 introduces a twist in the carbamate linkage; (2) whereas the data of Table III suggest a well-packed BDDAP-C-BHTCNQ molecule, Figure 13 shows a conformer in which the bis-hexyl “tails” are not well-aligned with each other; (3) whereas the crystal structure of BMAP-C-HMTCAQ (24) shows that both dicyanomethylene substituents on the anthracene ring deviate from the plane in the same direction, Figure 15 shows that MNDO gave them a “corkscrew” twist. The MNDO ionization energies I_D are probably 1–2 eV high, as expected from a Koopmans’ theorem calculation; the size of the difference $\Delta E = (I_D - A_A) - (I_A - A_D)$ is large, as expected. The calculated barrier for forward tunneling in BDDAP-C-FHTCNQ is

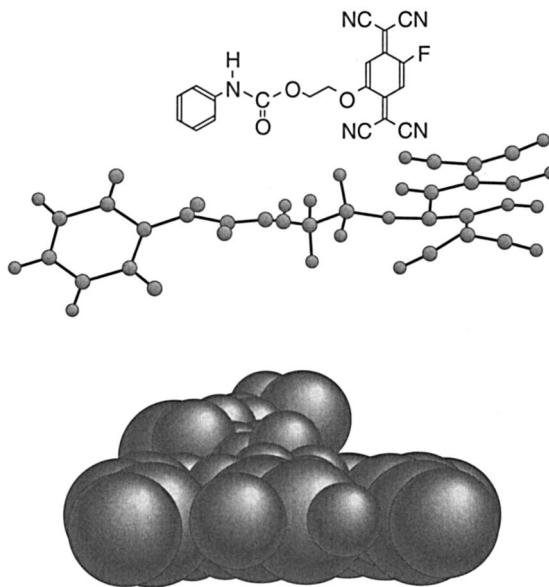


Figure 12. Structure (top) MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) for Ph-C-FHTCNQ, a variant of Ph-C-BHTCNQ, 59; $I_D = 9.141$ eV, $A_A = 2.941$ eV, $I_A = 9.555$ eV, $A_D = 0.062$ eV, $\Delta T_R = I_D - A_A = 6.200$ eV, $\Delta T_R = I_A - A_D = 9.493$ eV; $\Delta E = \Delta T_F - \Delta T_R = 3.293$ eV. (Reproduced with permission from reference 22. Copyright 1988.)

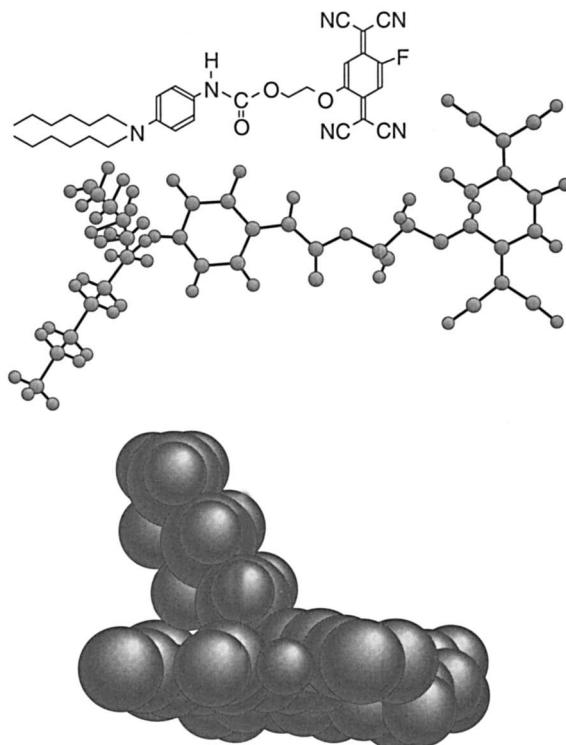


Figure 13. Structure (top), MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) for BHAP-C-BHTCNQ, a variant of BDDAP-C-BHTCNQ, 37; $I_D = 8.767 \text{ eV}$, $A_A = 2.936 \text{ eV}$, $I_A = 9.560 \text{ eV}$, $A_D = 0.099 \text{ eV}$; $\Delta T_F = I_D - A_A = 5.831 \text{ eV}$, $\Delta T_R = I_A - A_D = 9.461 \text{ eV}$; $\Delta E = \Delta T_F - \Delta T_R = 3.630 \text{ eV}$. (Reproduced with permission from reference 22. Copyright 1988.)

a very large $\Delta T_F \approx 5.8 \text{ eV}$, whereas for a real Aviram–Ratner rectifier one hopes $\Delta T_F \approx 1\text{--}3 \text{ eV}$.

Fourier Transform Infrared Spectra of D- σ -A Monolayers. Grazing-angle Fourier transform infrared spectra of monolayers of BDDAP-C-HMTCAQ, BDDAP-C-BHTCNQ, and TDDOP-C-HETCNQ have been measured and reported previously (21–23, 25). The C–H stretch bands are well-resolved, even for a single monolayer, and a broad structure at about 3500 cm^{-1} is seen for “fresh” samples, but disappears for samples older than about 60 days; this may be water trapped between the LB film layer and the aluminum substrate.

Nonlinear Optical Data on D- σ -A Systems. An attempt was made to see whether any second-harmonic signals could be detected

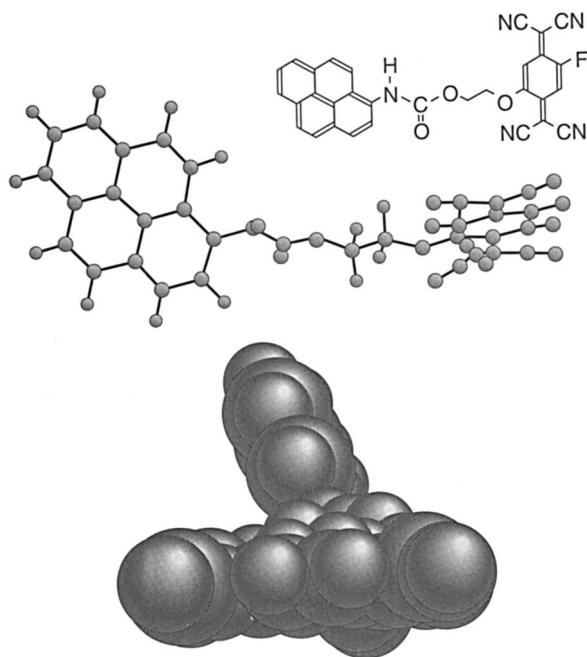


Figure 14. Structure (top), MNDO conformation (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom), for Py-C FHTCNQ, a variant of Py-C-BHTCNQ; 39; $I_D = 8.192$ eV, $A_A = 2.957$ eV, $I_A = 8.986$ eV, $A_D = 1.175$ eV; $\Delta T_F = I_D - A_A = 5.235$ eV; $\Delta T_R = I_A - A_D = 8.347$ eV; $\Delta E = \Delta T_F - \Delta T_R = 3.112$ eV. (Reproduced with permission from reference 22. Copyright 1988.)

from Z multilayers of **50**, but the result was negative, maybe because the Z-type multilayers may have reorganized with the time elapsed between deposition and measurement (Cephalas, A. C., personal communication).

The third-order nonlinear optical susceptibility $\chi^{(3)}$ was measured (very crudely) for dilute chloroform solutions of **42**, **48**, **49**, and **51** by the self-trapping of an Ar ion laser beam ($\lambda = 514.5$ nm). For two of them, the concentrations were measured, so that the molecular γ could also be measured. The results are as follows: **42**, $\chi^{(3)} = 2.5 \times 10^{-7}$ cm⁴ statC⁻²; **48**, $\chi^{(3)} = 6.8 \times 10^{-8}$ cm⁴ statC⁻²; **49**, $\chi^{(3)} = 1.1 \times 10^{-7}$ cm⁴ statC⁻², $\gamma = 1.45 \times 10^{-26}$ cm⁷ statC⁻²; and **51**, $\chi^{(3)} = 2.5 \times 10^{-6}$ cm⁴ statC⁻², $\gamma = 3.36 \times 10^{-24}$ cm⁷ statC⁻² (31). The values are quite large and probably incorporate solution heating effects and resonant enhancements due to molecular absorption bands. In particular, the ratio $\gamma(\mathbf{51})/\gamma(\mathbf{49}) = 231$ seems to be due to the presence of TCNQ in **51**, but not in **49**. In fact, a later experiment of degenerate

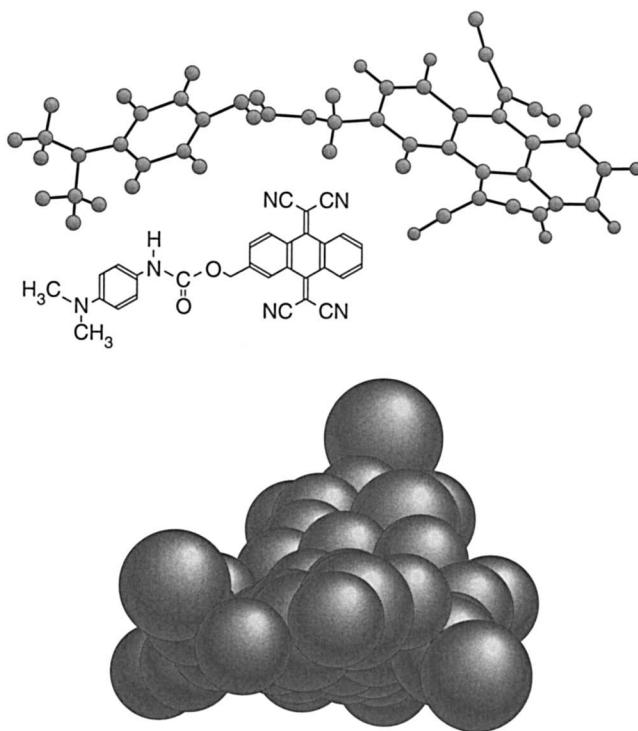


Figure 15. MNDO conformation (top), structure (middle), and MNDO van der Waals shape, viewed from the acceptor end (bottom) of DMAP-C-HMTCAQ, 60; $I_D = 9.052 \text{ eV}$, $A_A = 2.627 \text{ eV}$; $I_A = 9.364 \text{ eV}$, $A_D = 0.144 \text{ eV}$; $\Delta T_R = I_D - A_A = 6.425 \text{ eV}$, $\Delta T_R = I_A - A_D = 9.220 \text{ eV}$; $\Delta E = \Delta T_F - \Delta T_R = 2.795 \text{ eV}$. (Reproduced with permission from reference 22. Copyright 1988.)

four-wave mixing using frequency-doubled Nd-YAG beam ($\lambda = 532 \text{ nm}$) and the same solution of 51 destroyed the sample, because of absorption, obviously due to the TCNQ chromophore (205).

Rectification Experiments

Here we discuss seven attempts, by the ORP and by others, to detect rectification.

Macroscopic Test: Metal | Langmuir–Blodgett monolayer | Hg. In the first experiment (9), a 2-mm diameter droplet of Hg was used to probe the conductivity across a single monolayer LB film deposited on top of either Pt or conducting tin oxide (ITO) glass; three sandwiches were thus tested:

1. Pt|DDOP-C-BHTCNQ|Hg
2. Pt|Py-C-BHTCNQ|Hg
3. ITO|DDOP-C-BHTCNQ|Hg

In all cases the background conductivity of the solid support was measured, presumably because of microscopic pinholes in the LB film or because of damage to the film by the Hg drop (9).

Macroscopic Test: Al|BDDAP-C-BHTCNQ|Al Fingers with Low Overlap. In the hope that maybe defects may be avoided, statistically, in a domain of the order of about 0.5×0.5 mm, if one searched through enough samples, the left-hand half of 15 glass microscope slides was coated (using a mask) with five parallel fingers of Al at least 500-nm thick, 3.5-mm long, and 1.6-mm wide (21). Then the 15 slides were coated with a single LB monolayer of BDDAP-C-BHTCNQ, 37, at room temperature. Finally, the slides were coated again with five fingers of Al, but this time on the right-hand side of the slide, so that the vertical overlap Al|BDDAP-C-BHTCNQ|Al would be in an area of only about 0.5×0.5 mm. Of the 75 junctions thus prepared, many were open circuits; the rest were short circuits. Thus, a defect-free domain of BDDAP-C-BHTCNQ was not found (21).

Nanoscopic Test: STM on H Atom Switch. In 1988 (111) it was reported that rectification had been observed in a modified Digital Instruments Nanoscope I STM, for molecule 8, which had been originally designed as internal hydrogen atom transfer switch (and not as a rectifier). The claim for molecular rectification was later retracted (112).

Nanoscopic Test: STM on BDDAP-C-BHTCNQ. Pomerantz also kindly studied with his modified STM, an LB monolayer of BDDAP-C-BHTCNQ, 37, deposited on a Au|Ag|mica substrate, using an atomically sharp W tip, as the couple W|BDDAP-C-BHTCNQ|Au. Large “rectification” currents were observed (22, 23), but later control experiments by Pomerantz showed that this “rectification effect”, with very large currents, could also occur in the absence of any molecule. Disclaimers were issued (22, 23).

Macroscopic Test: Pt|DDOP-C-BHTCNQ|Mg|Al. Sambles and co-workers (42) at the University of Exeter found that a monolayer of DDOP-C-BHTCNQ, 38, sandwiched between Pt and Mg electrodes, behaved as a rectifying LB film. The great merit of this work was to have made defect-free LB monolayers, but the molecule used does not contain a strong donor moiety, that is, I_D is probably too high for an Aviram–Ratner rectifier. Indeed the rectifying behavior has been ascribed to Schottky barrier formation between Mg and TCNQ (44, 45).

Macroscopic Test: Pt| $C_{16}H_{33}\text{-Q3CNQ}|Mg|\text{Al}$. Later, Sambles' and Ashwell's group found that an LB film of *Z*-*b*-(1-hexadecyl-4-quinolinium)- α -cyano-4-styryldicyanometanide ($C_{16}H_{33}\text{-Q3CNQ}$, 20) similarly sandwiched between Pt and Mg electrodes (the Mg shadowed with Ag) also showed macroscopic rectification behavior (43). However, the observed current–voltage (*I*–*V*) curves may also be due to a Schottky barrier (Mg 3CNQ salt) (44).

Nanoscopic Test: STM on BDDAP-C-HETCNQ, Py-C-HETCNQ, and $C_{16}H_{33}\text{-Q3CNQ}$. With a Digital Instruments Nanoscope II STM, we have studied samples of BDDAP-C-HETCNQ (40) (31), Py-C-HETCNQ (41) (31), and $C_{16}H_{33}\text{-Q3CNQ}$ (20) (the latter kindly supplied by G. J. Ashwell) (205). The samples were transferred onto highly oriented pyrolytic graphite (Union Carbide grade ZYA and ZYH) by the LS horizontal transfer lifting technique and were studied in air at room temperature using Pt–Ir “nanotips” (Digital Instruments) and the “A” head. At low set-point currents, some asymmetries in the *I*–*V* plots could be seen. In preliminary work with BDDAP-C-HETCNQ and Py-C-HETCNQ, the image of graphite is replaced by what seems to be an image of the film (31). The images are shown in Figures 16–18. The substrate does not allow for easy transfer by the LB method, so the LS (horizontal lift) technique was used.

The images are not of graphite, and, in particular, the data of Figure 18 provide atomic resolution. It is likely that in Figures 16 and 17 the

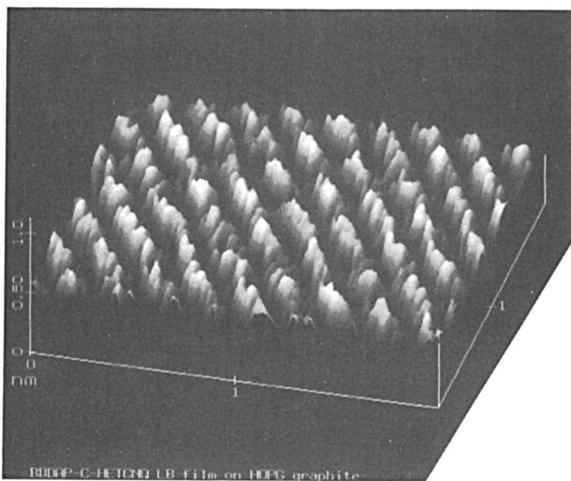


Figure 16. STM image (X, Y scan width 2 nm; Z height 1 nm) of BDDAP-C-HETCNQ, 40, on HOPG graphite; Pt–Ir tip. (Reproduced with permission from reference 31. Copyright 1991.)

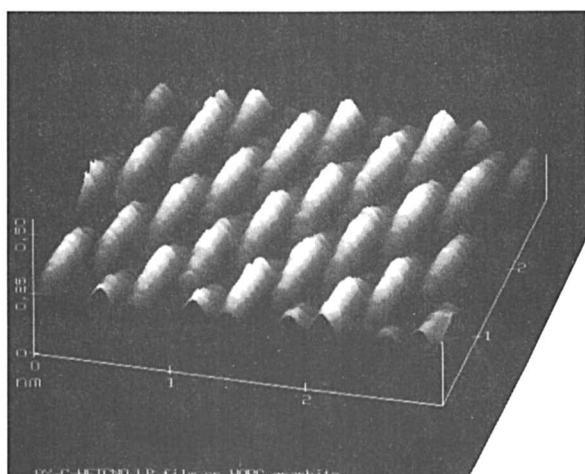


Figure 17. STM image (X, Y scan width 2 nm; Z height 1 nm) of Py-C-HETCNQ, 41, on HOPG graphite. Pt-Ir tip. (Reproduced with permission from reference 31. Copyright 1991.)

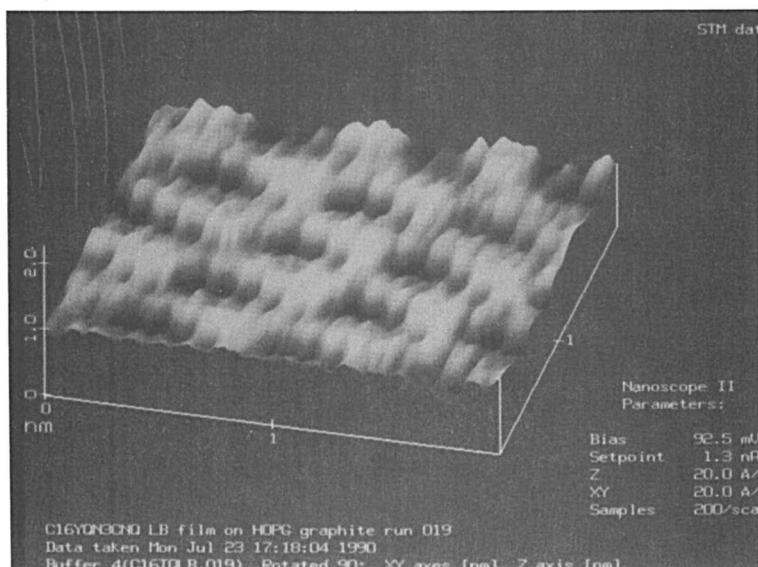


Figure 18. STM image (X, Y scan width 2 nm; Z height 1 nm) of C₁₆H₃₃-3CNQ, 20, on HOPG graphite. Pt-Ir tip (205).

Pt–Ir tip has penetrated partially through the monolayer, but it is not quite clear what molecular features are seen. Figure 18 can be interpreted by assuming that the hexadecyl “tail” of C₁₆H₃₃-Q3CNQ, **20**, is closest to the graphite, while the Pt–Ir tip “sees” the cyano atoms at the opposite end of the zwitterionic molecule. However, the LS transfer was not successful in a later experiment with **20**, and only the graphite surface was seen. Atomic resolution was not seen on a large-single-crystal-Au (111) surface, even after Ar⁺ ion milling and annealing at 500 °C. The same bad luck was had with Au on mica samples.

When the LS transfers of **20**, **21**, and **40** were successful, attempts were made to detect the rectification curve by using this capability in the STM software: The scan is interrupted, and a series of voltage pulses and increases in the tunneling current are collected and displayed; then the tunneling scan is resumed. Interesting hints of rectification were seen at different times, with all manner of asymmetric curves, but the effect was not seen reproducibly enough to inspire any confidence. Efforts are still continuing, with modifications to the STM head, new preparations of Au on mica (206), and so on.

Conclusion

The progress toward the organic rectifier has been reviewed, also in the broader perspective of other related issues in unimolecular electronics. Schottky barrier rectification has been seen in LB films of D- σ -A and D⁺- π -A⁻ molecules, but the goal of Aviram–Ratner rectification through an oriented D- σ -A molecule has not yet been achieved. Guidelines for future synthetic efforts and experimental tests have been discussed.

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References

1. Metzger, R. M. In *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Eds.; NATO ASI Series; Plenum: New York, 1991; Vol. B248, p 691.
2. Aviram, A.; Freiser, M. J.; Seiden, P. E.; Young, W. R. U.S. Patent 3 953 874, April 27, 1976.
3. Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* 1974, 29, 277.
4. Aviram, A.; Seiden, P. E.; Ratner, M. A. In *Molecular Electronic Devices*, Carter, F. L., Ed.; Dekker: New York, 1982; p 5.
5. Bagdadchi, J.; Panetta, C. A. *J. Org. Chem.* 1983, 48, 3852.
6. Metzger, R. M.; Panetta, C. A. *J. Phys. (Les Ulis, Fr.) Colloque* 1983, 44, C3-1605.
7. Metzger, R. M.; Panetta, C. A. In *Molecular Electronic Devices*, Carter, F. L., Ed.; Dekker: New York, 1987; Vol. 2, p 1.
8. Panetta, C. A.; Baghdadchi, J.; Metzger, R. M. *Mol. Cryst. Liq. Cryst.* 1984, 107, 103.
9. Metzger, R. M.; Panetta, C. A.; Heimer, N. E.; Bhatti, A. M.; Torres, E.; Blackburn, G. F.; Tripathy, S. K.; Samuelson, L. A. *J. Mol. Electron.* 1986, 2, 119.
10. Metzger, R. M.; Panetta, C. A.; Miura, Y.; Torres, E. *Synth. Metals* 1987, 18, 797.
11. Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* 1987, 52, 2944.
12. Metzger, R. M.; Panetta, C. A. In *Proceedings of the Eighth Winter Conference on Low-Temperature Physics*; UNAM: Mexico City, Mexico, 1987; p 81.
13. Laidlaw, R. K.; Miura, Y.; Panetta, C. A.; Metzger, R. M. *Acta Cryst.* 1988, C44, 2009.
14. Laidlaw, R. K.; Miura, Y.; Grant, J. L.; Cooray, L.; Clark, M.; Kispert, L. D.; Metzger, R. M. *J. Chem. Phys.* 1987, 87, 4967.
15. Laidlaw, R. K.; Baghdadchi, J.; Panetta, C. A.; Miura, Y.; Torres, E.; Metzger, R. M. *Acta Cryst.* 1988, B44, 645.
16. Miura, Y.; Laidlaw, R. K.; Panetta, C. A.; Metzger, R. M. *Acta Cryst.* 1988, C44, 2007.
17. Metzger, R. M.; Schumaker, R. R.; Cava, M. P.; Laidlaw, R. K.; Panetta, C. A.; Torres, E. *Langmuir* 1988, 4, 298.
18. Metzger, R. M.; Panetta, C. A. In *Organic and Inorganic Lower-Dimensional Materials*; Delhaès, P.; Drillon, M., Eds.; NATO ASI Series; Plenum: New York, 1988; Vol. B168, p 271.
19. Miura, Y.; Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* 1988, 53, 439.
20. Miura, Y.; Panetta, C. A.; Metzger, R. M. *J. Liq. Chrom.* 1988, 11, 245.
21. Metzger, R. M.; Panetta, C. A. *J. Mol. Electron.* 1989, 5, 1.
22. Metzger, R. M.; Panetta, C. A. *J. Chim. Phys.* 1988, 85, 1125.
23. Metzger, R. M.; Panetta, C. A. *Synth. Met.* 1989, 28, C807.
24. Metzger, R. M.; Laidlaw, R. K.; Torres, E.; Panetta, C. A. *J. Cryst. Spectr. Res.* 1989, 19, 475.

25. Metzger, R. M.; Panetta, C. A. In *Molecular Electronics—Science and Technology*; Aviram, A.; Bross, A., Eds., New York Engineering Foundation: New York, 1990; p 293.
26. Metzger, R. M.; Wiser, D. C.; Laidlaw, R. K.; Takassi, M. A.; Mattern, D. L.; Panetta, C. A. *Langmuir* **1990**, *6*, 1515.
27. Metzger, R. M.; Panetta, C. A. In *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Eds.; NATO ASI Series; Plenum: New York, 1991; Vol. B248, p 641.
28. Metzger, R. M.; Panetta, C. A. In *Advanced Organic Solid State Materials*; Chiang, L. Y.; Cowan, D. O.; Chaikin, P., Eds.; Materials Research Society Symposium Proceedings Series; Materials Research Society: Philadelphia, PA, 1990; Vol. 173, p 531.
29. Metzger, R. M.; Panetta, C. A. In *Condensed Systems of Low Dimensionality*; Beeby, J. L., Ed.; NATO Advanced Study Institute Series; Plenum: New York, 1991; Vol. B253, p 779.
30. Metzger, R. M.; Panetta, C. A. *New J. Chem.* **1991**, *15*, 209.
31. Metzger, R. M.; Panetta, C. A. *Synth. Met.* **1991**, *42*, 1407.
32. Panetta, C. A.; Heimer, N. E.; Hussey, C. L.; Metzger, R. M. *Synlett* **1991**, *301*.
33. Metzger, R. M., In *Molecular Electronics—Science and Technology*; Aviram, A., Ed.; American Institute of Physics Conference Proceedings; American Institute of Physics: New York, 1992; Vol. 262, p 85.
34. Torres, E.; Heimer, N. E.; Clark, B. J.; Hussey, C. L. *J. Org. Chem.* **1991**, *56*, 3737.
35. Blodgett, K. B. *J. Am. Chem. Soc.* **1935**, *57*, 1007.
36. Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964.
37. Gaines, G. L., Jr.; *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience: New York, 1966.
38. Kuhn, H.; Möbius, D.; Bücher, H. In *Physical Methods of Chemistry*, Vol. I, Part IIIB; Weissberger, A.; Rossiter, B. W., Eds.; Wiley: New York, 1972; p 577.
39. *Langmuir-Blodgett Films*; Roberts, G., Ed.; Plenum: New York, 1990.
40. Kuhn, H. *Pure Appl. Chem.* **1979**, *51*, 341.
41. Kuhn, H. *Pure Appl. Chem.* **1981**, *53*, 2105.
42. Geddes, N. J.; Sambles, J. R.; Jarvis, D. J.; Parker, W. G.; Sandman, D. J. *Appl. Phys. Lett.* **1990**, *56*, 1916.
43. Ashwell, G. J.; Sambles, J. R.; Martin, A. S.; Parker, W. G.; Szablewski, M. *J. Chem. Soc. Chem. Commun.* **1990**, 1374.
44. Sandman, D. J.; Laski, J.; Geddes, N. J.; Sambles, J. R.; Jarvis, D. J.; Parker, W. G. *Synth. Metals* **1991**, *42*, 1415.
45. Geddes, N. J.; Sambles, J. R.; Jarvis, D. J.; Parker, W. G.; Sandman, D. J. *J. Appl. Phys.*, in press.
46. Binnig, G.; Rohrer, H.; Gerber, Ch.; Weibel, E. *Phys. Rev. Lett.* **1982**, *49*, 57.
47. *Molecular Electronic Devices*; Carter, F. L., Ed.; Dekker: New York, 1982.
48. *Molecular Electronic Devices*; Carter, F. L., Ed.; Dekker: New York, 1987; Vol. II.
49. *Molecular Electronic Devices, Proceedings of the 3rd International Symposium*; Carter, F. L.; Siatkowski, R. E.; Wohltjen, H., Eds.; North-Holland: Amsterdam, The Netherlands, 1988.
50. *Molecular Electronics—IVth International School on Condensed Matter*; Borissov, M., Ed.; World Scientific: Singapore, 1987.

51. *Molecular Electronics—Science and Technology*; Aviram, A.; Bros, A., Eds.; New York Engineering Foundation: New York, 1990.
52. *Molecular Electronics—Science and Technology*; Aviram, A., Ed.; American Institute of Physics: New York, 1992; Vol. 262.
53. Haddon, R. C.; Lamola, A. C. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 1874.
54. Swalen, J. D.; Allara, D. L.; Andrade, J. D.; Chandross, E. A.; Garoff, S.; Israelachvili, J.; McCarthy, T. J.; Murray, R.; Pease, R. F.; Rabolt, J. F.; Wynne, K. J.; Yu, H. *Langmuir* **1987**, *3*, 932.
55. *Graphite Intercalation Compounds*; Davidov, D.; Selig, H., Eds.; Synthetic Metals Series; 1988; Vol. 23.
56. Acrivos, J. V. NATO ASI Series, 1984; Vol. C130, p 479.
57. For the proceedings of three recent conferences, see (a) *Advanced Organic Solid State Materials*; Chiang, L. Y.; Cowan, D. O.; Chaikin, P., Eds.; Materials Research Society Symposium Proceedings Series, MRS: Philadelphia, PA, 1990; Vol. 173; (b) *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Eds.; NATO ASI Series; Plenum: New York, 1991; Vol. B248; (c) *Synth. Met.* **1991**, *41–43*.
58. *Handbook of Conducting Polymers*, Skotheim, T. A., Ed.; Dekker: New York, 1986; Vol. I and II.
59. Relevant articles in *Extended Linear-Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1982, 1982, 1983; Vols. I, II, and III.
60. Inabe, T.; Hoshino, N.; Mitani, T.; Maruyama, Y. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2245.
61. Carter, F. L. In *Molecular Electronic Devices*; Carter, F. L., Ed.; Dekker: New York, 1982; p 51.
62. Fujihira, M.; Nishiyama, K.; Yamada, H. *Thin Solid Films* **1985**, *132*, 77.
63. Lehn, J.-M. *Angew. Chem. Intl. Ed. Engl.* **1988**, *27*, 89.
64. Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687.
65. Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7064.
66. Kenny, P. W.; Miller, L. L.; Rak, S. F.; Jozefiak, T. R.; Christopfel, W. C.; Kim, J. H.; Uphaus, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 4445.
67. Szejtli, J. *Cyclodextrin Technology*; Kluwer: Dordrecht, Holland, 1988.
68. *Calixarenes, a Versatile Class of Macroyclic Compounds*; Vicens, J.; Böhmer, V. Eds.; Kluwer: Dordrecht, Holland, 1990.
69. Enzel, P.; Bein, T. In *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Eds.; NATO ASI Series, Plenum: New York, 1991; Vol. B248, p 421.
70. Meinhard, J. E. *Appl. Phys. Lett.* **1964**, *35*, 3059.
71. Kinzig, B. J. In *Molecular Electronic Devices*; Carter, F. L., Ed.; Dekker: New York, 1982; p 223.
72. Langmuir, I.; Schaefer, V. J. *J. Am. Chem. Soc.* **1938**, *60*, 1351.
73. Mann, B.; Kuhn, H. *J. Appl. Phys.* **1971**, *42*, 4398.
74. Handy, R. M.; Scala, L. C. *J. Electrochem. Soc.* **1966**, *113*, 109.
75. Roberts, G. G.; Vincett, P. S.; Barlow, W. A. *J. Phys. C* **1978**, *11*, 2077.
76. Thredgold, R. H.; Vickers, A. J.; Allen, R. A. *J. Phys. D* **1984**, *17*, L5.
77. Peterson, I. R. *J. Chim. Phys.* **1988**, *85*, 997.
78. Polymeropoulos, E. E.; Möbius, D.; Kuhn, H. *Thin Solid Films* **1980**, *68*, 173.
79. Sugi, M.; Sakai, K.; Saito, M.; Kawabata, Y.; Iizima, S. *Thin Solid Films* **1985**, *132*, 69.

80. Potember, R. S.; Poehler, T. O.; Cowan, D. O. *Appl. Phys. Lett.* **1979**, *34*, 405.
81. Potember, R. S.; Hoffmann, R. C.; Hu, H. S.; Cocchiaro, J. E.; Viands, C. A.; Murphy, R. A.; Poehler, T. O. *Polymer* **1987**, *28*, 574.
82. Potember, R. S.; Hoffman, R. C.; Benson, R. C.; Poehler, T. O. *J. Phys. (Les Ulis) Colloque* **1983**, *44*, C3-1597.
83. Yamaguchi, S.; Viands, C. A.; Potember, R. S. *J. Vac. Sci. Technol. B* **1991**, *9*, 1129.
84. White, H. S.; Kittleson, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375.
85. Turner Jones, E. T.; Chyan, O. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 5526.
86. Paloheimo, J.; Kuivalainen, P.; Stubb, H.; Vuorimaa, E.; Yli-Lahti, P. *Appl. Phys. Lett.* **1990**, *56*, 1157.
87. Ryu, H.; Akagane, K.; Kori, H. *Chem. Econ. Eng. Rev.* **1986**, *18*(12), 26.
88. Slonim, J.; Mole, D.; Bauer, M. *Library Hi-Tech* **1985**, *3*(4), 27.
89. Kalanaraman, P. S.; Kuder, J. E.; Jones, R. S. In *Functional Polymers*; Bergbreiter, D. E.; Martin, C. R., Eds.; Plenum: New York, 1989; p 173.
90. Nikles, D. E.; Forbes, C. E.; Goldberg, H. A.; Johnson, R. E.; Kohn, R. S.; Onorato, F. J. *Proc. Soc. Photo-optical Instrum. Eng.* **1989**, *107B*, 43.
91. Ruaudel-Teixier, A.; Vandevyver, M.; Barraud, A. *Mol. Cryst. Liq. Cryst.* **1985**, *120*, 319.
92. Vandevyver, M. In *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Eds.; NATO ASI Series; Plenum: New York, 1991; Vol. B248, p 503.
93. Nakamura, T.; Tachibana, H.; Matsumoto, M.; Tanaka, M.; Kawabata, Y. In *Lower-Dimensional Systems and Molecular Electronics*; Metzger, R. M.; Day, P.; Papavassiliou, G. C., Eds.; NATO ASI Series; Plenum: New York, 1991; Vol. B248, p 519.
94. Coronel, P.; Barraud, A.; Claude, R.; Kahn, O.; Ruaudel-Teixier, A.; Zarembowitch, J. *J. Chem. Soc. Chem. Commun.* **1989**, 193.
95. Wasielewski, M. R.; Johnson, D. G.; Svec, W. A.; Kersey, K. M.; Cragg, D. E.; Minsek, D. W. In *Photochemical Energy Conversion*; Norris, J. R., Jr.; Meisel, D., Eds.; Elsevier: New York, 1989; p 135.
96. Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135.
97. Maoz, R.; Netzer, L.; Gun, J.; Sagiv, J. *J. Chim. Phys.* **1988**, *85*, 1059.
98. Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513.
99. Wilson, E. G. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 271.
100. Mueller, P.; Rubin, D. O.; Tien, H. T.; Wescott, W. C. *Nature (London)* **1962**, *194*, 979, and *J. Phys. Chem.* **1963**, *67*, 534.
101. Montal, M. *Annu. Rev. Biophys. Bioeng.* **1976**, *5*, 116.
102. Li, D.-Q.; Ratner, M. A.; Marks, T. J.; Zhang, C.-H.; Yang, J.; Wong, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7389.
103. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.
104. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 321.
105. Graff, G. *Science (Washington, D.C.)* **1991**, *254*, 1306.
106. Bedrossian, P.; Chen, D. M.; Mortensen, K.; Golovchenko, J. A. *Nature (London)* **1989**, *342*, 258.
107. Dunlap, D. D.; Bustamante, C. *Nature (London)* **1989**, *342*, 204.

108. Clemmer, C. R.; Beebe, Jr., T. P. *Science (Washington, D.C.)* **1991**, *251*, 640.
109. Ohmori, T.; Hashimoto, K.; Fujishima, A. *Jpn. J. Appl. Phys.* **1991**, *30*, 1826.
110. Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1.
111. Aviram, A.; Joachim, C.; Pomerantz, M. *Chem. Phys. Lett.* **1988**, *146*, 490.
112. Aviram, A.; Joachim, C.; Pomerantz, M. *Chem. Phys. Lett.* **1989**, *162*, 416.
113. Sixl, H.; Higelin, D. In *Molecular Electronic Devices*; Carter, F. L., Ed.; Dekker: New York, 1987; Vol. II, p 27.
114. Ulrich, K.; Port, H.; Wolf, H. C.; Wonner, J.; Effenberger, F.; Ilge, H.-D. *Chem. Phys.* **1991**, *154*, 311.
115. Tachibana, H.; Nakamura, T.; Matsumoto, M.; Komizu, H.; Manda, E.; Niino, H.; Yabe, A.; Kawabata, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3080.
116. Birge, R. R.; Cooper, T. M. *Biophys. J.* **1983**, *42*, 61.
117. Taube, H. *Pure Appl. Chem.* **1975**, *44*, 25.
118. Meyer, T. J. In *Photochemical Energy Conversion*, Norris, J. R., Jr.; Meisel, D., Eds.; Elsevier: New York, 1989; p 75.
119. Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 670.
120. Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.
121. Liang, N.; Miller, J. R.; Closs, G. L. *J. Am. Chem. Soc.* **1990**, *112*, 5353.
122. Marcus, R. A.; *Disc. Faraday Soc.* **1960**, *29*, 21.
123. Deisenhofer, J.; Epp, O.; Miki, K.; Huber, R.; Michel, H. *J. Mol. Biol.* **1984**, *180*, 385.
124. Arnoux, B.; Ducruix, A.; Reiss-Husson, F.; Kutz, M.; Norris, J.; Schiffer, M.; Chang, C. H. *FEBS Lett.* **1989**, *258*, 47.
125. Kirmaier, C.; Holten, D. *Biochemistry* **1991**, *30*, 609.
126. Kirmaier, C.; Holten, D.; Bylina, E. J.; Youvan, D. C. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 7562.
127. Breton, J.; Martin, J.; Fleming, G. R.; Lambray, J. *Biochemistry* **1988**, *27*, 8276.
128. Petrich, J. W.; Martin, J. L.; Houde, D.; Poyart, C.; Orszag, A. *Biochemistry* **1987**, *26*, 7914.
129. Kirmaier, C.; Holten, D.; Parson, W. W. *Biochim. Biophys. Acta* **1985**, *810*, 33.
130. Woodbury, N. W.; Becker, M.; Middendorf, D.; Parson, W. M. *Biochemistry* **1985**, *24*, 7516.
131. McIntosh, A. R.; Bolton, J. R.; Connolly, J. S.; Marsh, K. L.; Cook, D. R.; Ho, T.-F.; Weedon, A. C. *J. Phys. Chem.* **1986**, *90*, 5640.
132. Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090.
133. Nishitani, S.; Kurata, N.; Sakata, Y.; Misumi, S.; Karen, A.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1983**, *105*, 7771.
134. Osuka, A.; Nagata, T.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y. *Chem. Phys. Lett.* **1991**, *185*, 88.
135. Lindsay, J.; Mauzerall, D.; Linschitz, H. *J. Am. Chem. Soc.* **1983**, *105*, 6528.
136. Delaney, J. K.; Lindsay, J. S.; Mauzerall, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 957.
137. Krieger, C.; Weiser, J.; Staab, H. A. *Tetrahedron Lett.* **1985**, *26*, 6050.

138. Hush, N. S.; Paddon-Row, M. N.; Cotsaris, E.; Oevering, H.; Verhoeven, J. W.; Heppener, M. *Chem. Phys. Lett.* **1985**, *117*, 8.
139. Kroon, J.; Verhoeven, J. W.; Paddon-Row, M. N.; Oliver, A. M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1358.
140. Effenberger, F.; Wolf, H. C. *New. J. Chem.* **1991**, *15*, 117.
141. Moore, T. A.; Gust, D.; Mathis, P.; Mialocq, J.-C.; Chachaty, C.; Bensasson, R. V.; Land, E. J.; Doizi, D.; Liddell, P. A.; Lehman, W. R.; Nemweth, G. A.; Moore, A. L. *Nature (London)* **1984**, *307*, 630.
142. Gust, D.; Moore, T. A.; Moore, A. L.; Lee, S.-J.; Bittersman, E.; Luttrull, D. K.; Rehms, A. A.; DeGraziano, J. M.; Ma, X. C.; Gao, F.; Belford, R. E.; Trier, T. T. *Science (Washington, D.C.)* **1990**, *248*, 199.
143. Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991; Chapters 7 and 10.
144. Metzger, R. M.; Heimer, N. E.; Ashwell, G. J. *Mol. Cryst. Liq. Cryst.* **1984**, *107*, 133.
145. Akhtar, S.; Tanaka, J.; Metzger, R. M.; Ashwell, G. J. *Mol. Cryst. Liq. Cryst.* **1986**, *139*, 353.
146. Ashwell, G. J. U.K. Patent Appl. 9007230.7, 1990.
147. Ashwell, G. J.; Dawnay, E. J. C.; Kuczynski, A. P.; Szablewski, M. In *Advanced Organic Solid State Materials*; Chiang, L. Y.; Cowan, D. O.; Chaikin, P., Eds.; Materials Research Society Symposium Proceedings Series; Materials Research Society: Philadelphia, PA, 1990; Vol. 173, p 507.
148. Becker, J. Y.; Bernstein, J.; Bittner, S.; Levi, N.; Shaik, S. *J. Am. Chem. Soc.* **1983**, *105*, 4468.
149. Staab, H. A.; Hintz, R.; Knaus, G. H.; Krieger, C. *Chem. Ber.* **1983**, *116*, 2827.
150. Murata, I. *Pure Appl. Chem.* **1983**, *55*, 323.
151. (a) Wacks, M. E.; Dibeler, V. H. *J. Chem. Phys.* **1959**, *31*, 1557; (b) Wacks, M. E. *J. Chem. Phys.* **1964**, *41*, 1661.
152. Lichtenberger, D. L.; Johnston, R. L.; Hinkelmann, K.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1990**, *112*, 3302.
153. Dvorak, V.; Nemek, I.; Zyka, J. *Mikrochem. J.* **1967**, *12*, 324.
154. Batley, M.; Lyons, L. E. *Mol. Cryst. Cryst.* **1968**, *3*, 357.
155. Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, *87*, 513.
156. Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183.
157. Compton, R. N.; Cooper, C. D. *J. Chem. Phys.* **1977**, *66*, 4325.
158. Garron, R. C. *Rend. Acad. Sci. Paris* **1964**, *258*, 1458.
159. Grepstad, J. K.; Garland, P. O.; Slagsvold, B. J. *Surf. Sci.* **1976**, *57*, 348.
160. Potter, H. C.; Blakeley, J. M. *J. Vac. Sci. Technol.* **1975**, *12*, 635.
161. Demuth, J. E. *Chem. Phys. Lett.* **1977**, *45*, 12.
162. Matsen, F. A. *J. Chem. Phys.* **1956**, *24*, 602.
163. Hush, N. S.; Pople, J. A. *Trans. Faraday Soc.* **1955**, *51*, 600.
164. Pope, M. *J. Chem. Phys.* **1962**, *37*, 1001.
165. Kluge, W. In *Landolt-Börnstein Physikalische Tabellen*, 6th ed.; Springer: Berlin, Germany, 1959; Vol. 2, Part 6, p 909.
166. Jain, S. C.; Krishnan, K. S. *Proc. Roy. Soc. London* **1952**, *A213*, 143.
167. Green, D. C. *J. Org. Chem.* **1979**, *44*, 1476.
168. Hertler, W. R. *J. Org. Chem.* **1976**, *41*, 1412.
169. Baghdadchi, J. Ph.D. Dissertation, University of Mississippi, Dec. 1982.
170. Heimer, N. E., University of Mississippi, Unpublished results.
171. Kini, A. M.; Cowan, D. O.; Gerson, F.; Möckel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556.

172. Chen, W.; Cava, M. P.; Takassi, M. A.; Metzger, R. M. *J. Am. Chem. Soc.* **1988**, *110*, 7903.
173. Gleiter, R.; Schmidt, E.; Cowan, D. O.; Ferraris, J. P. *J. Electron. Spectrosc.* **1973**, *2*, 207.
174. Berlinsky, A.; Carolan, J. F.; Weiler, L. *Can. J. Chem.* **1973**, *52*, 3373.
175. Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2125.
176. Clar, E.; Robertson, J. M.; Schloegl, R.; Schmidt, W. *J. Am. Chem. Soc.* **1981**, *103*, 1320.
177. Cooper, C. D.; Naff, W. T.; Compton, R. N. *J. Chem. Phys.* **1975**, *63*, 2752.
178. Gutmann, F.; Lyons, L. E. *Organic Semiconductors*; Wiley: New York, 1967; p 698.
179. Hussey, C. L.; Baghdadchi, J.; Panetta, C. A.; Metzger, R. M., Unpublished results.
180. Takassi, M. A. Ph.D. Dissertation, University of Mississippi, Aug. 1989.
181. Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962**, *84*, 3370.
182. Wheland, R. C.; Gilsson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.
183. Anderson, J. R.; Jorgensen, O. *J. Chem. Soc. Perkin Trans. I* **1979**, 3095.
184. Emge, T. J.; Maxfield, McR.; Cowan, D. O.; Kistenmacher, T. *J. Mol. Cryst. Liq. Cryst.* **1981**, *65*, 161.
185. Eggins, B. R. *Chem. Commun.* **1969**, 1267.
186. Aumüller, A.; Hüning, S. *Liebigs Ann. Chem.* **1986**, 165.
187. Ashraf, M.; Headridge, J. B. *Talanta* **1969**, *16*, 1439.
188. Jeftic, L.; Manning, G. *J. Electroanal. Chem.* **1970**, *26*, 195.
189. Peover, M. E. *J. Chem. Soc.* **1962**, 4540.
190. Kuder, J. K.; Pochan, J. M.; Turner, S. R.; Hinman, D. F. *J. Electrochem. Soc.* **1978**, *125*, 1750.
191. Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.
192. Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Chesnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233.
193. Peover, M. E. *Trans. Faraday Soc.* **1962**, *58*, 2370.
194. Lyons, L. E.; Palmer, L. D. *Austr. J. Chem.* **1976**, *29*, 1919.
195. Farragher, A. L.; Page, F. M. *Trans. Faraday Soc.* **1967**, *63*, 2369.
196. Chowdhury, S.; Kebarle, P. *J. Am. Chem. Soc.* **1986**, *108*, 5453.
197. Miller, L. L.; Nordblum, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916.
198. Parker, V. D. *J. Am. Chem. Soc.* **1976**, *98*, 98.
199. Ebbersen, L. In *Advances in Physical Organic Chemistry*; Gold, V.; Bethell, D., Eds.; Academic: Orlando, FL, 1982; Vol. 18, p 79.
200. Nelsen, S. F. *Isr. J. Chem.* **1979**, *18*, 45.
201. Bechgaard, K.; Andersen, J. R. In *The Physics and Chemistry of Low-Dimensional Solids*; Alcácer, L., Ed.; NATO ASI Series, Reidel: Dordrecht, Holland, 1980; Vol. C56, p 247.
202. Wu, X.-L.; Parakka, J. L.; Metzger, R. M., Unpublished results.
203. Nadizadeh, H.; Mattern, D. L.; Singleton, J.; Wu, X.-L.; Metzger, R. M., Unpublished results.
204. Chandra Sekhar, P., Unpublished results.
205. Wu, X.-L.; Shamsuzzoha, M.; Metzger, R. M.; Ashwell, G. J., Submitted for publication in *Adv. Mater.*
206. Holland-Moritz, E.; Gordon, J., II; Borges, G.; Sonnenfeld, R. *Langmuir* **1991**, *7*, 301.

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