Langmuir-Blodgett Films of Donor-σ-Acceptor (D-σ-A) Compounds, Where D = Anilide Donors with Internal Diyne or Saturated Lipid Tails, σ = Carbamate Bridge, and A = 4-Nitrophenyl or TCNQ Acceptors†

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Several amphiphilic D-σ-A molecules were synthesized with three interlocked design criteria: they are potential rectifiers of electrical current, they possess one or two sturdy polymerizable diacetylene tails, and they may have interesting nonlinear optical properties. Most of the molecules afforded good self-assembling monolayers, one transferred well as a Langmuir-Blodgett film, and a few gave polymers that may be topotactic.

Introduction

To use a donor-σ-acceptor (D-σ-A) compound as a "molecular diode", i.e., as a molecule-sized rectifier of electrical current, one must first assemble a strong and ordered monolayer, with all molecules oriented in the same direction (Figure 1). Such a molecular rectifier, originally proposed by Aviram and Ratner,[1] would be the first and simplest "truly molecular device".[2] Evidence in support of current rectification by such molecules has recently appeared.[3,4] Long alkyl chains (lipid "tails") attached to one end of the D-σ-A molecules (Figure 1) aid[5,6] in the formation of well-oriented Pockels-Langmuir films at the air-water interface[7,8] and also facilitate the transfer of D-σ-A molecules to an electrode surface by the Langmuir-Blodgett (LB) technique.[9,10] LB films of some previously synthesized lipid-D-σ-A molecules lack adequate cohesion, as shown by defects (presumably pinholes) during attempted rectification experiments.[11,12]

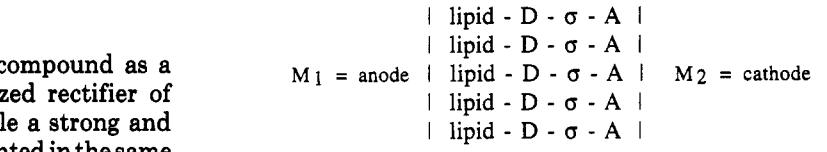

Figure 1. Schematic idea of Aviram-Ratner molecular diode or rectifier, formed by accosting two conventional metal films M_1 = "anode" and M_2 = "cathode" to an organized monolayer D-σ-A. The molecules D-σ-A form an LB film when transferred from the air-water interface either to a hydrophilic metal substrate M_2, or to a hydrophobic metal substrate M_1; the other metal is evaporated onto the organic layer. A lipid "tail" covalently bonded to the D end (as shown here) or to the A end may aid the monolayer self-assembly at the air-water interface. The donor part D is more easily oxidized to D^+ than it is reduced to D^-, and the acceptor part A is more easily reduced to A^- than it is oxidized to A^+. Therefore the zwitterionic excited state D^+-σ-A^- is lower in energy (by 3-5 eV) than the state D^--σ-A^+, and the energy barrier for through-bond electron transfer is much lower for D-σ-A → D^+-σ-A^- than for D-σ-A → D^--σ-A^+. In the illustration above, the easy direction for electron transfer is from M_2 to M_1. The covalently bonded "bridge" σ serves to separate the molecular orbitals of D from those of A. The lipid tail may slow down the electron transfer.

In an attempt to avoid such defects, we decided to incorporate conjugated diacetylene groups within the alkyl tails. Such diyne groups undergo polymerization upon UV irradiation,[13] which should fix a Langmuir monolayer into a covalently bonded sheet, thus creating a stronger film.[14,15] A second long-range goal for this project was to polymerize the diacetylene-containing molecules topotactically, if possible, so that these D-σ-A-functionalized, diacetylene-polymer LB films could be used as either frequency doublers (high $\chi^{(2)}$) or as frequency triplers (high $\chi^{(3)}$) of electromagnetic radiation, in line with previous nonlinear optical work on polydiacetylene LB films.[13-15]

We describe here the preparation and Langmuir film properties of several D-σ-A compounds, **1a-g** (Figure 2),

† Dedicated to the memory of Dr. Yasuhiro Kawabata (1947-1991).

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(1) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277-283.
(2) Metzger, R. M.; Panetta, C. A. *New J. Chem.* **1991**, *15*, 209-221.
(3) Geddes, N. J.; Sambles, J. R.; Jarvis, D. J.; Parker, W. G.; Sandman, D. J. *Appl. Phys. Lett.* **1990**, *56*, 1916.
(4) Martin, A. S.; Sambles, J. R.; Ashwell, G. J. *Phys. Rev. Lett.* **1993**, *70*, 218-221.
(5) Metzger, R. M.; Schumaker, R. R.; Cava, M. P.; Laidlaw, R. K.; Panetta, C. A.; Torres, E. *Langmuir* **1988**, *4*, 298-304.
(6) Metzger, R. M.; Wiser, D. C.; Laidlaw, R. K.; Takassi, M. A.; Mattern, D. L.; Panetta, C. A. *Langmuir* **1990**, *6*, 350-357.
(7) Kuhn, H. In Weissberger, A., Rossiter, B. W., Eds.; *Physical Methods of Chemistry*; Wiley-Interscience: New York, 1971; Vol. 1, p 581.
(8) Roberts, G., Ed.; *Langmuir-Blodgett Films*; Plenum: New York, 1990.
(9) Blodgett, K. B. *J. Am. Chem. Soc.* **1935**, *57*, 1007-1022.
(10) Blodgett, K. B.; Langmuir, I. *Phys. Rev.* **1937**, *51*, 964-982.
(11) Metzger, R. M.; Panetta, C. A. *J. Mol. Electron.* **1988**, *5*, 1-16.
(12) 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*, 119-124.
(13) Wegner, G. *Pure Appl. Chem.* **1977**, *49*, 443-454.
(14) Tieke, B.; Lieser, G. *J. Colloid Interface Sci.* **1982**, *88*, 471-486.
(15) Day, D. R.; Ringsdorf, H. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 205.

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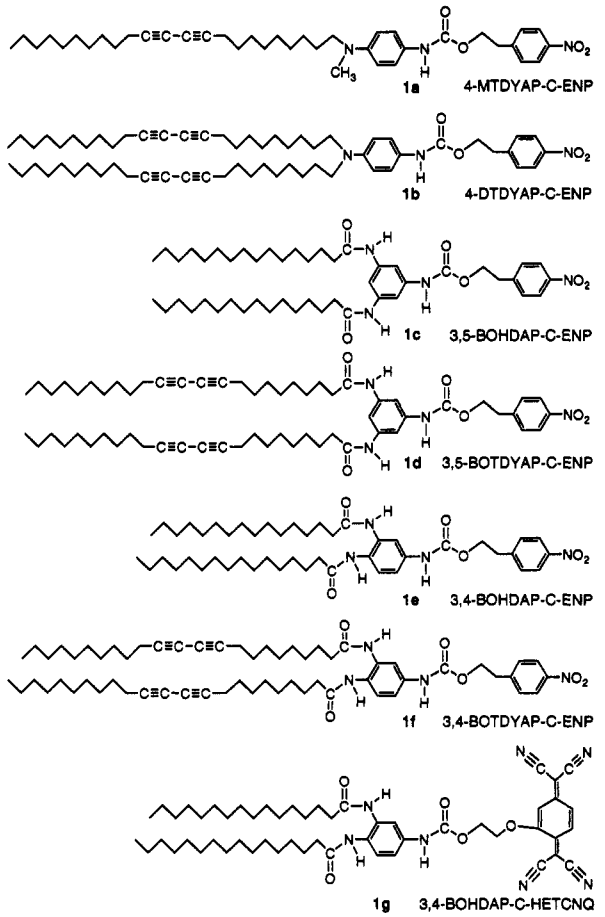


Figure 2. Target molecules: **1a**, **1b**, **1d**, and **1f** are the diacetylenes; **1c**, **1e**, and **1g** are models with alkyl tails. Compounds **1a–1g** have been given slightly different acronyms elsewhere: the old acronyms were **1a** = MTDAP-C-ENP,[17,18] **1c** = 3,5-BHDOAP-C-ENP,[20] **1d** = 3,4-BTDYOAP-C-ENP,[19,20] **1e** = 3,4-BHDOAP-C-ENP,[19,20] **1f** = 3,5-BTDYOAP-C-ENP,[19,20] and **1g** = 3,4-BHDOAP-C-HETCNQ.[19,20]

containing one or two lipid "tails". These tails are either derivatives of the conjugated diacetylene 10,12-tricosadiyne or, as initial model compounds, saturated alkanes. The donors (D) are carbamate anilides, with either an additional amine group or two amido groups. The insulating sigma bridge (σ) is a carbamate linkage with a $-CH_2CH_2-$ tether to the acceptor. The acceptor (A) is the model system 4-nitrophenyl, except for **1g**, which contains the strong one-electron acceptor TCNQ.[16]

The LB film formation has been summarized before,[17–20] as were preliminary $\chi^{(3)}$ values;[17] here we provide a full account of the synthesis and details of all the measurements.

Synthetic Strategies

Preparation of the Diyne Tail (Figure 3). The 10,12-tricosadiynyl group served as a lipid tail with a conjugated diacetylene at midchain. Introduction of this group into the donor anilines required either the corresponding aldehyde **7** (for reductive amination attachment) or the acid chloride **17** (for amidation attachment); both were prepared from 10,12-tricosadiynoic acid, **5**.

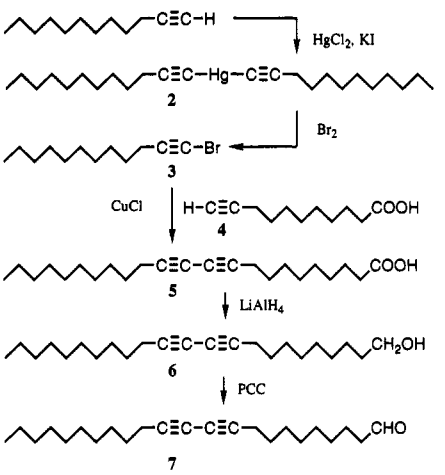


Figure 3. Synthesis of diynal **7**.

Construction of the diyne linkage of **5** was done by the Cadiot–Chodkiewicz reaction.[21] This reaction couples a 1-bromo-1-alkyne with a terminal alkyne in the presence of catalytic CuCl; hydroxylamine is used as a reducing agent to maintain a low concentration of copper(I) ion. Attempted preparation of the required 1-bromo-1-dodecyne (**3**) by treatment of 1-dodecyne with aqueous sodium hypobromite[22] was unsuccessful, presumably because the reaction mixture was not homogeneous. Therefore, 1-dodecyne was treated with $HgCl_2$ and KI in alkaline MeOH[23] to form the crystalline mercury(II) salt **2**. This salt was dissolved in warm CCl_4 and treated with Br_2[21] to give **3**. (When reaction was attempted with an inhomogeneous mixture at room temperature, partial addition of Br_2 to the triple bond occurred.) Cadiot–Chodkiewicz coupling of **3** with 10-undecynoic acid (**4**) gave the conjugated diacetylene acid **5**.[24] The white crystals of **5** turned sky blue on standing, especially in light, indicating polymerization.[25] Blue samples could be purified by dissolving the acid in ether and filtering off the resulting red tarry suspension of polymer.

Acid **5** was reduced with $LiAlH_4$ to form alcohol **6**. No reduction of triple bonds was observed. Pyridinium chlorochromate (PCC) oxidized **6** to aldehyde **7**. (A modified procedure[26] in which the PCC is ground with silica gel helped to prevent overoxidation.) Compound **7** was not isolated; it solidified on exposure to air, forming a blue solid (presumably polymerized **5**) and was therefore stored for short periods in ether before use.

Attachment of Lipid Tails to Aniline Donors by Reductive Amination (Figures 4 and 5). Reductive amination was first performed on diyne aldehyde **7**, which was treated with 4-aminobenzoic acid (**8**) in the presence of $NaBH_3CN$ to provide monoalkylated amino acid **9**. Compound **9** precipitated, allowing its separation from

(16) Compton, R. N.; Cooper, C. D. *J. Chem. Phys.* **1977**, *66*, 4325–4329.
(17) Metzger, R. M.; Panetta, C. A. In Aviram, A., Brossi, A., Eds.; *Molecular Electronics—Science and Technology*; Engineering Foundation: New York, 1989; p 293.
(18) Metzger, R. M.; Panetta, C. A. In Metzger, R. M., Day, P., Papavassiliou, G. C., Eds.; *Lower-Dimensional Systems and Molecular Electronics* (*NATO ASI Series*); (Plenum: New York, 1991; B248, 611.
(19) Metzger, R. M.; Panetta, C. A. *Synth. Met.* **1991**, *42*, 1407.
(20) Metzger, R. M. Submitted to Birge, R. R., Ed.; *Biomolecular Electronics* (*ACS Symposium Series*).
(21) Eglington, G.; McCrae, W. *Adv. Org. Chem.* **1963**, *4*, 252–277.
(22) Straus, F.; Kollek, L.; Hauptmann, H. *Chem. Ber.* **1930**, *63*, 1868–1885.
(23) Johnson, J. R.; McEwan, W. N. *J. Am. Chem. Soc.* **1926**, *48*, 469–476.
(24) Tieke, B.; Wegner, G.; Naegele, D.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 764–765.
(25) Patal, G. N.; Yang, N.-L. *J. Chem. Educ.* **1983**, *60*, 181–185.
(26) Adams, L. L.; Luzzio, F. A. *J. Org. Chem.* **1989**, *54*, 5387–5390.

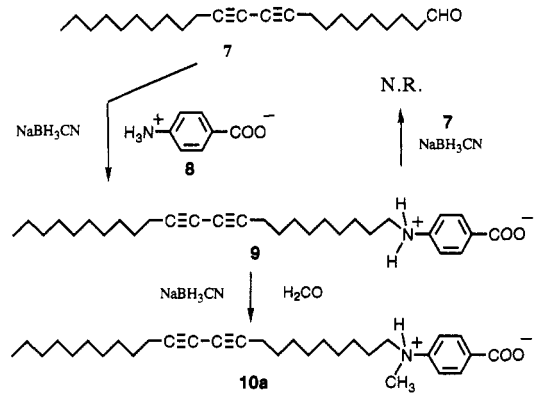


Figure 4. Synthesis of diyne aniline 10a.

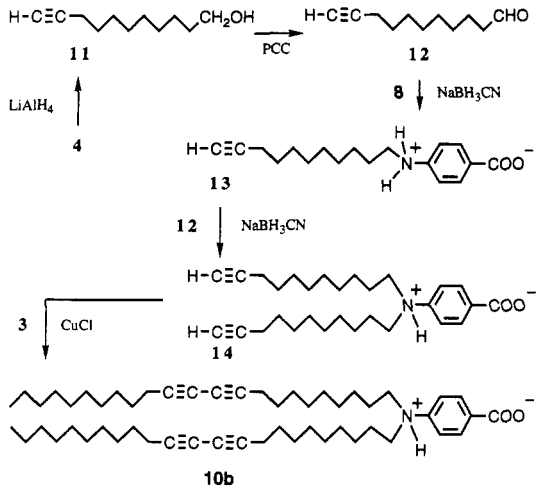


Figure 5. Synthesis of bisdiyne aniline 10b.

byproduct alcohol 6 which was formed by reduction of 7. An *N*-methyl group was then introduced by the reductive amination of 9 with formaldehyde.[27] The resulting donor 10a, with one diyne tail, turned light purple on standing, indicating polymerization.

We intended to construct a donor with two diyne tails in a similar fashion by alkylating 9 with a second molecule of 7. Although two decyl chains could be attached in this fashion, all attempts to prepare 10b by double reductive amination failed. The low solubility of 9 in MeOH may have hindered the reaction; THF was added to form a homogeneous solution but THF is not a good solvent for $NaBH_3CN$. As an alternate approach (Figure 5), 10-undecynoic acid (4) was reduced to alcohol 11 with $LiAlH_4$; 11 was then oxidized to aldehyde 12 and aminated with 8 to form monoalkylated amino acid 13. A second reductive amination of 12 with 13 formed dialkylated 14. This compound, now with two terminal acetylene tails, was coupled to two molecules of 1-bromo-1-dodecyne (3) by the Cadiot–Chodkiewicz method to form the desired product 10b.

We attempted to form 16, a donor with four diyne tails, by reductive amination of four equivalents of aldehyde 7 with 3,5-diaminobenzoic acid (15) or its methyl ester (Figure 6). TLC monitoring indicated several product spots (one, two, three, or four chains could in principle add to the substrate), but attempts to purify products by column chromatography resulted only in decomposition. Similar results were obtained with the saturated aldehyde

(27) Borch, R. F.; Hassid, A. I. *J. Org. Chem.* 1972, *37*, 1673–1674.

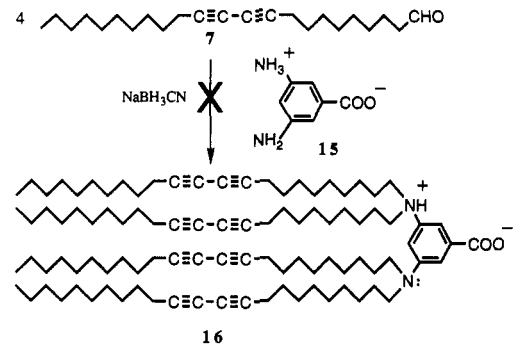


Figure 6. Failure to obtain 16 from 7.

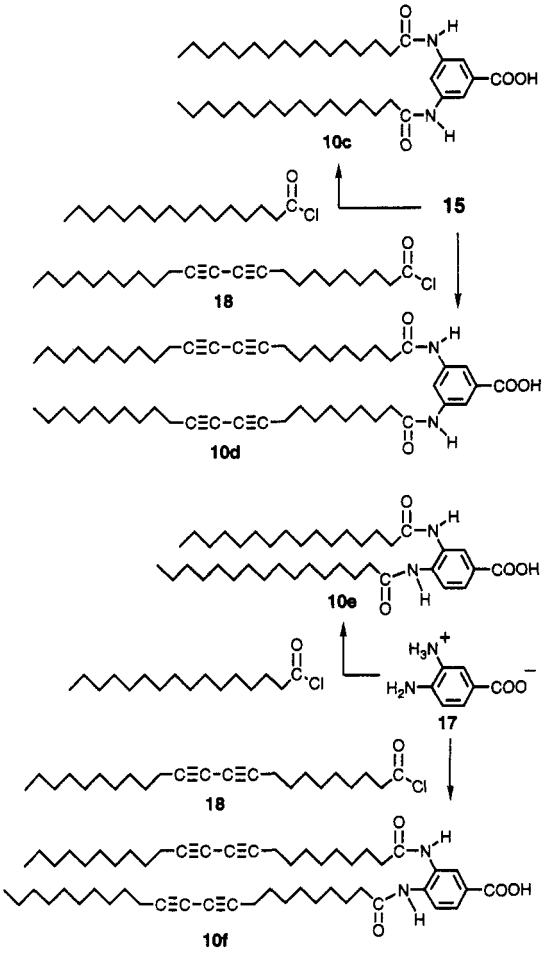


Figure 7. Synthesis of bisamides 10c–f.

decanal, showing that the problem was with 15 rather than with the diyne tails. Similar attempts to polyalkylate 3,4-diaminobenzoic acid (17) also failed.

Attachment of Lipid Tails to Aniline Donors as Amides (Figure 7). Since the amino groups of 15 and 17 could not be successfully alkylated with diyne tails, we decided to try to attach lipid tails as amides. A model saturated acyl chain, hexadecanoyl, was examined first; hexadecanoyl chloride acylated 15 in the presence of Et_3N in DMF solution to form 3,5-bisamide 10c as a high-melting solid. Preparation of the corresponding 3,5-bisamide with diyne tails, 10d, required the acid chloride 18 of 10,12-tricosadiynoic acid 5, which was prepared by treating 5 with $SOCl_2$. Compound 18 in $CHCl_3$ was then added to 15 in DMF, in the presence of Et_3N, to afford bisamide 10d.

Donors with amide tails in the 3,4 positions were

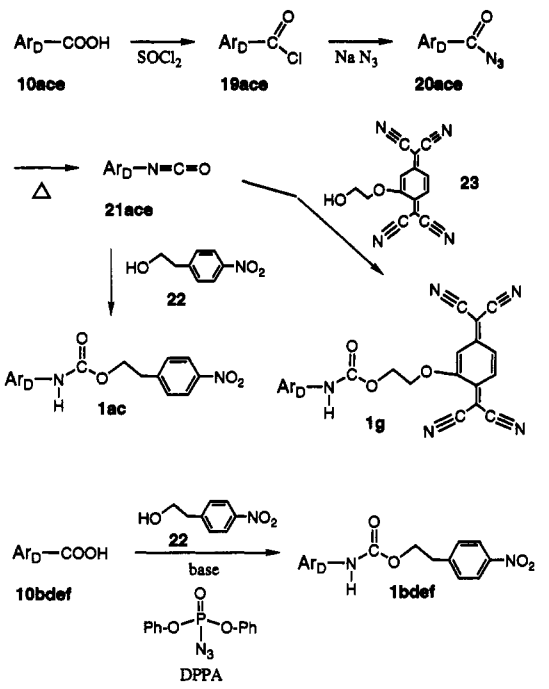


Figure 8. Carbamate coupling to yield **1a–g**.

prepared in a similar manner. Model compound **10e**, with C_{16}-saturated amides, was soluble only in warm aprotic solvents (dioxane, DMF, DMSO). In contrast to the 3,5 isomer with two diyne tails (**10d**), the 3,4 isomer (**10f**) was not very stable. It had a wide melting point range, turned gray upon attempted drying, and underwent color change on standing. However, the NMR spectrum of material purified by column chromatography and crystallized from MeOH confirmed the structure.

Attempts to synthesize a tetraamido four-chain donor from 3,4-bisamido **10e**, using DMSO anion to deprotonate the amides before adding acid chloride, were unsuccessful, perhaps due to the insolubility of **10e**.

Carbamate Coupling of Donor and Acceptor (Figure 8). Lipid-tailed donor acids **10a**, **10c**, and **10e** were coupled to acceptors by the Curtius rearrangement.[28] Each sample of **10** was treated with $SOCl_2$ to produce an acid chloride **19**, which was then treated with sodium azide to form acyl azide **20**. (There was no side reaction of diyne π bonds with sodium azide, a possible complication that may have thwarted model reactions with terminal alkene π bonds.) Heating **20** effected its Curtius rearrangement to isocyanate **21**. Treatment of **21a** or **21c** with the acceptor alcohol **22** in the presence of catalytic dibutyltin dilaurate[29] joined together the donor and acceptor with a carbamate σ bridge, forming lipid–D–σ–A products **1a** and **1c**.

Several attempts to prepare the isocyanate of the bisdiyne amine donor **10b** by classical Curtius rearrangement failed. We therefore turned to an alternate procedure: the conversion of carboxylic acids and alcohols directly to carbamates with diphenylphosphoryl azide (DPPA) and Et_3N.[30] This reaction is also believed to proceed through the acyl azide and isocyanate. D–σ–A compound **1b** was obtained after 1 day. Compound **1b** was purified by column chromatography but was not very stable; it was characterized by its IR and NMR spectra but did not give a satisfactory combustion analysis.

The DPPA procedure was more convenient than the classical Curtius sequence, and it was used to prepare D–σ–A compound **1d** from the 3,5-bis(diyne amide) **10d**. (The 3,5-bisamide with saturated tails, **10c**, could be converted to **1c** using DPPA, but the classical sequence was cleaner and was preferred.) The 3,4-bis(saturated amide) **10e** was converted with DPPA to D–σ–A compound **1e**; in this case, Et_3N was not effective as a base (the two amide nitrogens weaken the carboxyl acidity) and potassium *tert*-butoxide was used; also, DMF was required as a cosolvent with dioxane to achieve dissolution of **10e**. Coupling of 3,4-bis(diyne amide) **10f** with DPPA formed the D–σ–A carbamate **1f**.

Carbamate with TCNQ Acceptor. Several coupling reactions of donor with TCNQ–alcohol **23**[31] were attempted. Diyne amino donor **10a** was treated with **23** and DPPA. No product formation was observed by TLC; instead, the red color of TCNQ changed to green, indicating reduction of TCNQ to its radical anion (perhaps by Et_3N), and insoluble layers formed indicating polymerization. DPPA coupling of the 3,4-bis(saturated amide) **10e** to **23** also failed. Traditional Curtius rearrangement (Figure 8) was, however, successful in converting **10e** to a deep purple solution which yielded a black powder, **1g**, after column chromatography and crystallization from hexanes. Compound **1g** had appropriate IR peaks (shift of nitrile absorption to lower frequency and carbamate carbonyl); the NMR spectrum showed broad peaks for all aromatic and adjacent protons, which is apparently characteristic of this type of D–σ–A molecule.[12] As we have observed before with D–σ–A derivatives containing TCNQ,[6,12] a satisfactory combustion analysis could not be obtained, indicating relative instability of the compound.

Synthetic Details

General Procedures. Starting materials were from Aldrich. Dry solvents and chromatography solvents were distilled and stored over activated molecular sieves. TLC was performed on silica gel polyester plates with UV phosphor (Aldrich or Sigma). The developing solvent was 65:35 petroleum ether:EtOAc unless otherwise noted; the solvent "A" ratio was 55:45, "B" was 30:40, "C" was 50:50. Visualization was by iodine vapor, UV absorption, or $KMnO_4$ spray. Flash chromatography was carried out on EM Keiselgel 60 silica gel, 230–400 mesh; gravity chromatography was performed on Davisil silica gel, 100–200 mesh. The eluent was petroleum ether with an increasing gradient of EtOAc. Melting points were determined on a Mel-Temp apparatus and are uncorrected. ^1H NMR spectra were determined with a Bruker AC-E 300 spectrometer. Mass spectra were determined with a Hewlett-Packard 5985 GC/MS instrument (heated probe). IR spectra (KBr pellet) were determined with a Perkin Elmer FT-IR 1600 spectrometer. Elemental analyses were carried out by Desert Analytics, Tuscon, AZ.

Di-1-dodecynylmercury(II) (2). $HgCl_2$ (3.30 g, 12.2 mmol) and KI (8.10 g, 48.8 mmol) were dissolved in warm H_2O (8 mL), and 7.0 mL of 10% NaOH was added. While stirring, 1-dodecyne (1.66 g, 10.0 mmol) in 50 mL of EtOH was added dropwise over 45 min. The mercury salt precipitated and was collected by vacuum filtration and washed several times with cold EtOH. Recrystallization from EtOAc gave white needles of **2**, 2.44 g (92%): mp 88.5–89.5 °C (lit.[32] mp 84.5 °C); TLC R_f 0.57; IR (KBr) 2970, 2940, 2860, 2160, 1475, 1455, 1420 cm^{-1}; ^1H NMR

(28) Smith, P. A. S. *Org. React.* **1975**, *3*, 337–449.
(29) Francis, T.; Thorne, M. P. *Can. J. Chem.* **1976**, *54*, 24–30.
(30) Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* **1972**, *94*, 6203–6205.
(31) Miura, Y.; Torres, E.; Panetta, C. A.; Metzger, R. M. *J. Org. Chem.* **1988**, *53*, 439–440.
(32) Vaughn, T. *J. Am. Chem. Soc.* **1933**, *55*, 3453–3458.

($CDCl_3$) δ 2.25 (4H, t, $CH_2C{\equiv}C$), 1.5 (4H, quintet, $CH_2CC{\equiv}C$), 1.3 (28H, m, CH_2), 0.90 (6H, CH_3); MS, *m/z* 165 (M − Hg).

1-Bromo-1-dodecyne (3). A solution of Br_2 (6.02 g, 37.6 mmol) in 50 mL of CCl_4 was added slowly over 45 min to a solution of **2** (9.98 g, 18.8 mmol) in 500 mL of warm CCl_4. $HgCl_2$ precipitated. After the mixture was stirred for 15 min, the solvent was removed by rotary evaporation, and the product was extracted with chilled petroleum ether. The extract was passed through a short silica gel column (15 g), and the resulting crude product was vacuum distilled to afford 8.00 g (87%) of colorless **3**:[33] bp 76 °C (0.025 Torr) (lit.[33] bp 119–121 °C [1 Torr]); TLC R_f 0.68; IR (neat) 2920, 2860, 1220, 1470, 1430, 1325, 1110, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (2H, t, $CH_2C{\equiv}CBr$), 1.5 (2H quintet, $CH_2CC{\equiv}CBr$), 1.30 (14H, m, CH_2), 0.90 (3H, t, CH_3); MS, *m/z* 245 (M^+).

10,12-Tricosadiynoic Acid (5). The reaction apparatus was wrapped in foil to minimize photopolymerization of the product. 10-Undecynoic acid (**4**, 1.09 g, 6.00 mmol) was neutralized under N_2 with 10% KOH; then 20.0 mg (0.290 mmol) of hydroxylamine hydrochloride was added, followed by 0.100 g (0.600 mmol) of copper(I) chloride dissolved in 3.0 mL of 70% aqueous propylamine. To this yellow mixture was added **3** (0.980 g, 4.00 mmol) in 10 mL of MeOH, dropwise and very slowly. Whenever the mixture turned from yellow to green, a few drops of 10% aqueous hydroxylamine hydrochloride were added to restore the yellow color. The mixture was stirred for 30–45 min following the addition and then was neutralized with 1 N H_2SO_4 and extracted with ether (1 × 75, 3 × 25 mL), and the combined ether layers were dried over $MgSO_4$ and concentrated by rotary evaporation. The crude product was crystallized from petroleum ether to afford 0.990 g (71%) of **5**, a white solid which turned sky blue immediately upon exposure to air (before subsequent use, **5** was purified by dissolving in ether and removing the tarry impurities by filtration); mp 55.5–56.6 °C (lit.[24] mp 56.5 °C); TLC R_f 0.50; IR (KBr) 3000–2500 (broad), 2940, 2860, 1710, 1465, 1420, 1300, 1270, 940, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (2H, t, CH_2COO), 2.25 (4H, t, $CH_2C{\equiv}C$), 1.65 (2H, quintet, CH_2CCOO), 1.50 (4H, quintet, $CH_2CC{\equiv}C$), 1.35 (22H, m, CH_2), 0.90 (3H, t, CH_3); MS, *m/z* 346 (M^+).

10,12-Tricosadiyn-1-ol (6). To a stirred solution of $LiAlH_4$ (0.104 g, 2.76 mmol) in 60 mL of absolute ether was added, dropwise under N_2, **5** (0.692 g, 2.00 mmol) in 20 mL of ether. The mixture was gently refluxed until TLC indicated reaction was complete. Water was added cautiously and the mixture was poured into 100 mL of ice water and acidified with 10% H_2SO_4. The ether layer was separated and the aqueous layer was extracted with ether (3 × 30 mL). The combined ether layers were washed with 10% Na_2CO_3 and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the crude product was crystallized from petroleum ether to give 0.650 g (98%) of alcohol **6** as a white solid: mp 49–50 °C (lit.[34] mp 49 °C); TLC R_f 0.35; IR (KBr) 3400 (broad), 2970, 2860, 2220, 1460, 1370, 1310, 1110, 1050, 950 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (2H, t, CH_2O), 2.25 (4H, $CH_2C{\equiv}C$), 1.60–1.30 (31H, m, CH_2 + OH), 0.90 (3H, t, CH_3).

10,12-Tricosadiynal (7). In a flask equipped with a $CaSO_4$ drying tube was suspended pyridinium chlorochromate (PCC, 0.980 g, 4.60 mmol) in 10 mL of dry CH_2Cl_2. Compound **6** (1.30 g, 3.92 mmol) in 5 mL of CH_2Cl_2 was added in one portion. The orange mixture turned black and was stirred at room temperature for 1.5 h. Anhydrous ether (25 mL) was added, and the organic layer was decanted from the black gum. The undissolved residue was extracted with ether (3 × 25 mL). The combined ether layers were passed through a short silica gel column (15 g). Infrared spectroscopy of the eluent revealed the disappearance of the OH band (3500 cm^{-1}) and appearance of a C=O band (1730 cm^{-1}). Since the isolated aldehyde was not stable, it was kept in ether solution and used directly for the next step.

4-(10,12-Tricosadiynylamino)benzoic Acid (9). To a solution of 1.41 g (10.3 mmol) of 4-aminobenzoic acid (**8**) in 5 mL of dry MeOH was added **7** (prepared from 3.92 mmol of **6**) and, in small portions, 0.190 g (3.00 mmol) of $NaBH_3CN$. AcOH (0.5 mL) was added, and the reaction mixture was stirred at room temperature for 4 h. The resulting white precipitate was collected by vacuum filtration and was heated in 15 mL of H_2O on a steam bath for 30–45 min. The mixture was cooled and the product was filtered and crystallized from MeOH to give 1.22 g (69%) of **9** as a white solid: mp 114.5–115.5 °C; TLC R_f 0.18; IR (KBr) 2920, 2850, 1665, 1600, 1460, 1410, 1340, 1280, 1170, 835, 770, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (2H, d, Ar-H), 6.55 (2 H, d, Ar-H), 3.20 (2H, t, CH_2-N), 2.25 (4H, t, $CH_2C{\equiv}C$), 1.65 (2H, quintet, CH_2CN), 1.50 (4H, quintet, $CH_2CC{\equiv}C$), 1.40 (26H, m, CH_2 + N^+H_2), 0.90 (3H, t, CH_3); MS, *m/z* 451 (M^+). Anal. Calcd: C, 79.77; H, 10.04; N, 3.10. Found: C, 79.88; H, 10.26; N, 3.09.

4-[Methyl-(10,12-tricosadiynyl)amino]benzoic Acid (10a). To a stirred solution of **9** (0.270 g, 0.600 mmol) in 6 mL of dry CH_3CN was added 0.50 mL (6.00 mmol) of 40% aqueous formaldehyde in 3 mL of CH_3CN, followed by 0.114 g (1.80 mmol) of $NaBH_3CN$. AcOH (0.2 mL) was then added over 10 min. After 15 min, excess $NaBH_3CN$ was neutralized with dilute HCl and the mixture was extracted four times with ether. The combined organic layers were dried over $MgSO_4$. The solvent was removed by rotary evaporation and the resulting solid was crystallized from MeOH to afford 0.220 g (78%) of **10a** as a white solid which became light purple immediately upon exposure to air (**10a** was dissolved in dry ether and filtered to remove tarry impurities before use in the preparation of **1a**); mp 77–78 °C; TLC R_f 0.20; IR (KBr) 2920, 2850, 1665, 1600, 1525, 1460, 1415, 1385, 1340, 1300, 1185, 825, 765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59 (2H, d, Ar-H), 6.65 (2H, d, Ar-H), 3.40 (2H, t, CH_2N), 3.05 (3H, s, CH_3N), 2.25 (4H, t, $CH_2C{\equiv}C$), 1.60 (6H, m, $CH_2CC{\equiv}C$ + CH_2CN), 1.35 (25H, m, CH_2 + CH_2 + NH^+), 0.90 (3H, t, CH_3C); MS, *m/z* 465 (M^+). Anal. Calcd: C, 79.95; H, 10.17; N, 3.01. Found: C, 80.18; H, 10.14; N, 2.97.

10-Undecynol (11) was prepared from 10-undecynoic acid (**4**) using the procedure given above for **6**; vacuum distillation gave 85% of **11** as a colorless liquid: bp 99 °C (0.40 Torr) (lit.[35] bp 138 °C [14 Torr]); TLC (B) R_f 0.35; IR (neat) 3919, 3310, 2926, 2861, 2356, 2117, 1464, 1431, 1056, 721, 630 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.65 (2H, t, CH_2O), 2.2 (2H, dxt, $CH_2C{\equiv}C$), 1.95 (1H, t, $HC{\equiv}C$), 1.55 (5H, m, CH_2COH + $CH_2CC{\equiv}C$), 1.35 (10H, m, CH_2); MS, *m/z* 151 (M − OH).

10-Undecynal (12). PCC (1.54 g, 7.14 mmol) was ground with 1.50 g of silica gel. This mixture was suspended in 5.0 mL of dry CH_2Cl_2 in a flask equipped with a $CaSO_4$ drying tube. A solution of **11** (0.800 g, 4.76 mmol) in 5.0 mL of dry CH_2Cl_2 was added in one portion; the orange mixture changed to black. After 1.5 h, 25 mL of anhydrous ether was added and the organic layer was decanted. The remaining black gum was triturated with ether (3 × 20 mL) and the combined ether layers were passed through a short silica gel column (20 g). The IR spectrum of the eluent showed the loss of the OH group and the appearance of the aldehyde C=O. To avoid oxidation of the aldehyde, the product was kept in ether solution and directly used for the next step.

4-(10-Undecynylamino)benzoic Acid (13). Reductive amination of **12** (2.5 mmol) with **8** (10.0 mmol) and $NaBH_3CN$ (2.5 mmol) proceeded as described above for **9**; the crude product was crystallized from MeOH to afford 88% of **13** as a white solid: mp 116–118 °C; TLC R_f 0.25; IR (KBr) 3400, 2940, 2860, 2570, 2120, 1665, 1600, 1530, 1500, 1420, 1360, 1310, 1290, 1170, 840, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (2H, d, Ar-H), 6.55 (2H, d, Ar-H), 3.15 (2H, d, CH_2-N), 2.20 (2H, dxt, $CH_2C{\equiv}C$), 1.95 (1H, t, $HC{\equiv}C$), 1.65 (2H, quintet, CH_2CN), 1.55 (2H, quintet, CH_2-$CC{\equiv}C$), 1.4 (12H, m, CH_2 + N^+H_2); MS, *m/z* 287 (M^+). Anal. Calcd: C, 75.22; H, 8.77; N, 4.87. Found: C, 75.50; H, 8.84; N, 4.86.

4-(Di-10-undecynylamino)benzoic Acid (14). Compound **13** (0.530 g, 1.85 mmol) was dissolved in 15 mL of dry MeOH and 2 mL of dry THF. To this mixture was added aldehyde **12** (2.50 mmol based on **11**) followed by 0.116 g (1.85 mmol) of $NaBH_3CN$ and 0.20 mL of AcOH. The mixture was stirred for 8 h. When the reaction showed no further improvement by TLC, dilute HCl was added and the mixture was extracted with ether (1 × 50, 3 × 25 mL). The combined organic layers were dried over

(33) Remizova, L. A.; Kryukov, A. V.; Balova, I. A.; Favorskaya, I. A. *Zh. Org. Khim.* **1985**, *21*, 1001–1004.

(34) Tieke, B.; Lieser, G.; Wegner, G. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1631–1644.

(35) Miyaura, N.; Suginome, H.; Suzuki, A. *Tetrahedron* **1983**, *39*, 3271–3277.

anydrous $MgSO_4$. The mixture was flash chromatographed (50 g silica gel) to remove unreacted **13** and **11** formed by reduction of **12**, giving 0.560 g (69%) of **14** as a white solid: mp 31–32 °C; TLC R_f 0.35; IR 3307, 2929, 2855, 2668, 2117, 1911, 1670, 1600, 1556, 1527, 1413, 1287, 1185, 830, 773 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (2H, d, Ar-H), 6.60 (2H, d, Ar-H), 3.30 (4H, t, CH_2N), 2.20 (4H, dxt, $CH_2C{\equiv}C$), 1.95 (2H, t, $HC{\equiv}C$), 1.60 (8H, m, $CH_2CC{\equiv}C + CH_2CN$), 1.35 (21H, m, CH_2 + HN); MS, m/z 437 (M^+). Anal. Calcd: C, 79.58; H, 9.90, N, 3.20. Found: C, 79.68; H, 9.98; N, 3.20.

4-(Di-10,12-tricosadiynylamino)benzoic Acid (10b). Cadiot–Chodkiewicz coupling of **14** (1.6 mmol) and **3** (3.2 mmol) was performed as described above for **5**. (In some experiments, an excess of **3** was used to complete the reaction.) The crude product showed three spots on TLC. A fraction of the mixture (200 mg) was flash chromatographed (15 g silica gel) to give 86 mg (51%) of **10b** as a white solid (which turned to pink after a few days): mp 42–43 °C; TLC R_f 0.45; IR 2919, 2851, 1666, 1601, 1532, 1461, 1420, 1323, 1297, 1184, 938, 830, 759, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (2H, d, Ar-H), 6.60 (2H, d, Ar-H), 3.40 (4H, t, CH_2N), 2.25 (8H, t, $CH_2C{\equiv}C$), 1.60 (12H, m, $CH_2CC{\equiv}C + CH_2CN$), 1.35 (49H, m, CH_2 + N^+H), 0.90 (6H, t, CH_3). Anal. Calcd: C, 83.08, H, 10.92; H, 1.83. Found: C, 82.82; H, 10.91, N, 1.86.

3,5-Bis(1-oxohexadecylamino)benzoic Acid (10c). In a flask equipped with a $CaSO_4$ drying tube were placed 1.00 g (6.60 mmol) of 3,5-diaminobenzoic acid (**15**) and 2.02 g (20.0 mmol) of Et_3N in 25 mL of DMF. Palmitoyl chloride (5.50 g, 20.0 mmol) was added slowly and the mixture was stirred for 24 h, during which time a precipitate formed. The white solid was collected by vacuum filtration, washed with H_2O and cold MeOH, and crystallized from MeOH to afford 3.42 g (82%) of **10c**: mp 190–192 °C; TLC (A) R_f 0.25; IR (KBr) 3337, 2917, 2850, 1700, 1675, 1600, 1559, 1545, 1437, 1308, 1203, 1097, 887, 780, 720 cm^{-1}; ^1H NMR (DMSO) δ 10.0 (2H, s, NH), 8.20 (1H, s, Ar-H), 7.90 (2H, s, Ar-H), 2.30 (4H, t, CH_2-CO), 1.70 (4H, quintet, CH_2-C-CO), 1.35 (48H, m, CH_2), 0.85 (6H, t, CH_3). Anal. Calcd: C, 74.47, H, 10.89, N, 4.45. Found: C, 73.94; H, 10.80; N, 4.50.

3,5-Bis(1-oxo-10,12-tricosadiynylamino)benzoic Acid (10d). To a solution of 1.10 g (3.20 mmol) of **5** in 25 mL of dry CH_2Cl_2 was added 1 mL of freshly distilled $SOCl_2$ under N_2. After 6 h of reflux, the solvent was removed *in vacuo* and the residue was dissolved in 25 mL of dry $CHCl_3$. A solution of **15** (0.240 g, 1.60 mmol) and Et_3N (0.320 g, 3.20 mmol) in 5 mL of dry DMF was then added and the mixture was stirred for 24 h. The $CHCl_3$ was removed by rotary evaporation and water was added, followed by extraction with ether (1 × 50 mL, 3 × 25 mL). The combined ether layers were dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation to afford a crude oil. A portion (0.500 g) was flash chromatographed on silica gel (25 g) to afford 0.280 g (80%) of **10d** as a white powder: mp 161–165 °C; TLC R_f 0.35; IR (KBr) 3312, 2923, 2852, 1696, 1670, 1600, 1538, 1441, 1323, 1302, 1215, 1112, 1025, 907, 882, 774, 718 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.05 (2H, s, NH), 8.20 (1H, s, Ar-H), 7.90 (2H, s, Ar-H), 2.30 (12H, m, $CH_2CO + CH_2C{\equiv}C$), 1.70 (4H, quintet, CH_2CCO), 1.30 (52H, m, $CH_2CC{\equiv}C + CH_2$), 0.80 (6H, t, CH_3). Anal. Calcd: C, 78.66; H, 9.96; N, 3.46. Found: C, 78.44; H, 10.04; N, 3.58.

3,4-Bis(1-oxohexadecylamino)benzoic Acid (10e). In a flask equipped with a $CaSO_4$ drying tube were placed 1.00 g (6.58 mmol) of 3,5-diaminobenzoic acid (**18**) and 1.30 g (13.2 mmol) of Et_3N in 25 mL of DMF. Palmitoyl chloride (3.56 g, 13.2 mmol) in 5 mL of DMF was added slowly and the mixture was stirred for 2 h. The resulting precipitate was collected by vacuum filtration and washed with MeOH and water. This compound was insoluble in common solvents at room temperature but was soluble in hot aprotic solvents (DMF, DMSO, dioxane). It was crystallized from dioxane to afford 3.14 g (77%) of **10e** as a white powder: mp 195–197 °C; TLC R_f 0.25; IR (KBr) 3312, 2918, 2850, 1685, 1654, 1602, 1521, 1432, 1313, 1209, 1094, 881, 772, 714 cm^{-1}; ^1H NMR (warm DMSO) δ 9.30 (2H, s, NH), 8.10 (1H, s, Ar-H), 7.70 (2H, t, ArH), 2.35 (4H, t, CH_2CO), 1.65 (4H, quintet, CH_2CCO), 1.25 (48H, m, CH_2), 0.85 (6H, t, CH_3). Anal. Calcd: C, 74.47; H, 10.89; N, 4.45. Found: C, 74.66; H, 11.15; N, 4.59.

3,4-Bis(1-oxo-10,12-tricosadiynylamino)benzoic Acid (10f). Compound **5** (2.64 g, 7.60 mmol) in 10 mL of $CHCl_3$ and 0.1 mL of DMF was treated with 1.0 mL of $SOCl_2$ as described above for **10d**. A solution of 0.200 g (1.22 mmol) of **18** in 5 mL of DMF was added to the neat acid chloride, followed by 0.760 g (7.60 mmol) of Et_3N. After stirring for 30 h, the mixture was poured into water and extracted with ether (1 × 50 mL, 3 × 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed by rotary evaporation to yield 3.16 g of a crude oil. A portion (1.0 g) was flash chromatographed on silica gel (50 g). Two compounds were isolated (0.290 g), with TLC (A) R_f 0.45 and 0.60. Chromatography was repeated (10 g of silica gel) to afford 0.240 g of **10f**, R_f 0.45. Crystallization from MeOH gave 200 mg (20%) of a white solid which decomposed on standing: mp 172–173 °C; IR (KBr) 3316, 2918, 2854, 1696, 1670, 1600, 1533, 1449, 1329, 1218, 1117, 1025, 911, 887, 776, 713 cm^{-1}; ^1H NMR (DMSO-d_6) δ 10.05 (2H, s, NH), 8.20 (1H, s, Ar-H), 7.90 (2H, br, Ar-H), 2.30 (12H, m, $CH_2CO + CH_2C{\equiv}C$), 1.70 (4H, quintet, CH_2CCO), 1.30 (52H, m, $CH_2CC{\equiv}C + CH_2$), 0.80 (6H, t, CH_3).

Curtius Rearrangements. In a flask equipped with a $CaSO_4$ drying tube was placed donor acid **10** in benzene; some benzene was distilled off to dry the apparatus. About 2 mL of $SOCl_2$ (freshly distilled from 5% raw linseed oil) was added, and the reaction mixture was refluxed. After about 4 h, the IR spectrum of the mixture showed the loss of the carboxylate peak (1670 cm^{-1}) and the appearance of two peaks (1750 and 1720 cm^{-1}) for acid chloride **19**. The solvent and excess $SOCl_2$ were removed *in vacuo*, and the resulting oil was dissolved in 3:1 CH_3CN:THF. A 3-fold excess of sodium azide was added, and the mixture was stirred overnight. IR spectroscopy showed loss of the acid chloride carbonyl peaks and the appearance of two peaks (2140 and 1675 cm^{-1}) for acyl azide **20**. The solvent was removed by rotary evaporation and the resulting solid was washed with dry benzene and filtered to remove excess NaN_3. The filtrate was refluxed overnight to complete the Curtius rearrangement to **21**. The IR spectrum showed the loss of the azide bands and the appearance of the isocyanate peak for **21** (2280 cm^{-1}).

The solvent was removed by rotary evaporation and the resulting isocyanate, 1–2 equiv of 2-(4-nitrophenyl)ethanol (**22**), and 20 μL of dibutyltin dilaurate were dissolved under N_2 in dry THF. After 24 h, IR showed the loss of the isocyanate band and appearance of the carbamate carbonyl at 1705 cm^{-1}. Solvent was removed by rotary evaporation to afford crude product.

2-(4-Nitrophenyl)ethyl 4-[Methyl(10,12-tricosadiynyl)amino]phenylcarbamate (4-MTDYAP-C-ENP, 1a). The crude product was passed through a gravity silica gel column, from which a 10% yield of **1a** (last band of 4, TLC R_f 0.2) was isolated as a white solid: mp 78–80 °C; IR (KBr) 3360, 2930, 2860, 1690, 1600, 1525, 1460, 1340, 1250, 1080, 860, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.15 (2H, d, Ar-NO_2), 7.40 (2H, d, Ar-NR), 7.20 (2H, br, Ar-NR), 6.65 (2H, d, Ar-NO_2), 6.35 (1H, br, NH), 4.40 (2H, t, $COOCH_2$), 3.25 (2H, t, CH_2N), 3.10 (2H, t, CH_2ArNO_2), 2.90 (3H, s, CH_3N), 2.25 (4H, t, $CH_2C{\equiv}C$), 1.4 (6H, m, $CH_2CC{\equiv}C + CH_2CN$), 1.30 (26H, m, CH_2), 0.85 (3H, t, CH_3C); MS, m/z 463 ($M^+ - OCH_2CH_2$ $ArNO_2$). Anal. Calcd: C, 74.36; H, 8.80; N, 6.67. Found: C, 74.34; H, 8.76; N, 6.53.

2-(4-Nitrophenyl)ethyl 3,5-Bis[(1-oxohexadecyl)amino]phenylcarbamate (3,5-BOHDAP-C-ENP, 1c). Bisamide **10c** was dissolved in 3:1 CH_2Cl_2:$CHCl_3$ for the $SOCl_2$ reaction. The crude product was crystallized from MeOH to afford an 83% yield of light-brown **1c**: mp 148–149 °C; IR (KBr) 3299, 2922, 2853, 1697, 1667, 1601, 1558, 1440, 1308, 1218, 1107, 1013, 901, 874, 771, 714 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.30 (2H, d, $ArNO_2$), 7.60 (1H, s, Ar-H), 7.45 (2H, s, NHCO), 7.40 (2H, d, Ar–NO_2), 7.35 (2H, s, ArH), 6.90 (2H, s, CONH), 4.40 (2H, t, CH_2OCO), 3.10 (2H, t, CH_2ArNO_2), 2.30 (4H, t, CH_2CON), 1.65 (4H, quintet, CH_2CCON), 1.30 (48H, m, CH_2), 0.90 (6H, t, CH_3). Anal. Calcd: C, 71.17; H, 9.66; N, 7.06. Found: C, 71.09; H, 9.84; N, 7.03.

2-[[3,6-Bis(dicyanomethylene)-1,4-cyclohexadien-1-yl]oxy]ethyl 3,4-Bis[(1-oxohexadecyl)amino]phenylcarbamate (3,4-BOHDAP-C-HETCNQ, 1g). Bis-amide **10e** was dissolved in CH_2Cl_2 for the $SOCl_2$ reaction; 1:2 CH_3CN:THF was used for making **20e**. Isocyanate **21e** was treated with 0.5 equiv of TCNQ–alcohol **23**[31] rather than **22**. TLC (C) showed two colored products (R_f 0.20 and 0.30). The crude product was flash chromatographed (70 parts of silica gel) to give 39% of a dark brown solid which was crystallized from hexanes to afford a 28% yield of a black

powder which decomposed slowly on standing: TLC R_f 0.2; IR (CH_2Cl_2) 3252, 2922, 2208, 1699, 1670, 1600, 1530, 1453, 1340, 954, 900, 830 cm^{-1}; ^1H NMR ($CDCl_3$) broad peaks from aromatic and adjacent protons with no apparent splitting (as is the case for similar compounds[12]).

Carbamate Formation with DPPA. Donor acid **10** was dissolved in dry dioxane. Et_3N (1 equiv) was added, followed by 1 equiv of diphenylphosphoryl azide (DPPA) and 1.5–2.0 equiv of **22**. The mixture was refluxed under N_2 for 1 day. Water was added and the solution was extracted with ether (4 × 20 mL). The combined ether layers were dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the resulting oil was flash chromatographed (60 parts of silica gel).

2-(4-Nitrophenyl)ethyl 4-(Di-10,12-tricosadiynylamino)-phenylcarbamate (4-DTDYAP-C-ENP, 1b). Acid **10b** yielded 22% of **1b**. All attempts to crystallize this compound were unsuccessful; it decomposed on standing. TLC R_f 0.25; IR (neat) 3302, 2926, 2854, 1702, 1600, 1517, 1465, 1345, 1226, 1080, 856, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.20 (2H, d, $ArNO_2$), 7.45 (2H, br, ArNR), 7.15 (2H, br, ArNR), 6.60 (2H, d, $ArNO_2$), 6.30 (1H, br, NH), 4.40 (2H, t, $COOCH_2$), 3.25 (4H, t, CH_2N), 3.10 (2H, CH_2-$ArNO_2$), 2.25 (8H, t, $CH_2C{\equiv}C$), 1.60 (12H, m, $CH_2CC{\equiv}C + CH_2$-CN), 1.30 (48H, m, CH_2R), 0.90 (6H, t, CH_3).

2-(4-Nitrophenyl)ethyl 3,5-Bis[(1-oxo-10,12-tricosadiyn-yl)amino]phenylcarbamate (3,5-BOTDYAP-C-ENP, 1d). The crude oil from **10d** solidified during washing with petroleum ether. Crystallization from MeOH gave a 57% yield of a white solid: mp 104–105 °C; TLC (A) R_f 0.55; IR (KBr) 3299, 2926, 2854, 1698, 1663, 1602, 1558, 1430, 1307, 1215, 1006, 852, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.20 (2H, d, $ArNO_2$), 7.65 (1H, s, Ar-H), 7.45 (2H, s, Ar-H), 7.40 (2H, Ar-NO_2), 7.30 (2H, s, NH-CO), 6.85 (1H, s, NHCOO), 4.40 (2H, t, CH_2OCO), 3.10 (2H, t, CH_2ArNO_2), 2.30 (12H, m, $CH_2CO + CH_2C{\equiv}C$), 1.70 (4H, quintet, CH_2CCO), 1.55 (8H, quintet, $CH_2CC{\equiv}C$), 1.40 (44H, m, CH_2), 0.85 (6H, t, CH_3). Anal. Calcd: C, 75.27; H, 9.11; N, 5.76. Found: C, 75.33; H, 9.32; N, 5.51.

2-(4-Nitrophenyl)ethyl 3,4-Bis[(1-oxohexadecyl)amino]-phenylcarbamate (3,4-BOHDAP-C-ENP, 1e). The reaction mixture for donor **10e** turned cloudy when carried out as described above, but investigation by TLC showed no product formation. Potassium *tert*-butoxide (1 equiv) was therefore added, followed by addition of DMF to dissolve the mixture. After 2 days of reflux, the flask was cooled, and the resulting precipitate was collected, washed with hexane, and recrystallized from dioxane to afford a 70% yield of **1e** as a light-brown solid: mp 168–169 °C; TLC (A) R_f 0.45; IR (KBr) 3331, 2923, 2853, 1699, 1678, 1603, 1557, 1547, 1434, 1306, 1205, 1097, 887, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.30 (3H, d, $ArNO_2$ + NHCO), 7.99 (1H, s, NHCO), 7.45 (1H, s, Ar-H), 7.40 (2H, d, $ArNO_2$), 7.20 (1H, d, Ar-H), 7.10 (1H, d, Ar-H), 6.80 (1H, s, NHCOO), 4.40 (2H, t, CH_2OCO), 3.10 (2H, t, CH_2ArNO_2), 2.35 (4H, t, CH_2CON), 1.75 (4H, quintet, CH_2-$CCON$), 1.30 (48H, m, CH_2), 0.90 (6H, t, CH_3). Anal. Calcd: C, 71.17; H, 9.66; N, 7.06. Found: C, 71.14; H, 9.85; N, 7.04.

2-(4-Nitrophenyl)ethyl 3,4-Bis[(1-oxo-10,12-tricosadiyn-yl)amino]phenylcarbamate (3,4-BOTDYAP-C-ENP, 1f). Donor **10f** was dissolved in 50 parts of DMF for DPPA coupling. The crude oil was flash chromatographed (40 parts of silica gel) to obtain a 28% yield of **1f** as a light-brown solid: mp 132–133 °C; TLC (A) R_f 0.40; IR (KBr) 3288, 2924, 2854, 1700, 1663, 1604, 1552, 1436, 1356, 1243, 1023, 854, 726 cm^{-1}; ^1H NMR (DMSO-d_6) δ 8.25 (3H, t, $ArNO_2$ + NHCO), 8.05 (1H, s, NHCO), 7.45 (3H, t, $ArNO_2$ + Ar-H), 7.30 (1H, d, Ar-H), 7.25 (1H, s, Ar-H), 6.80 (1H, s, NHCOO), 4.40 (2H, t, CH_2OCO), 3.15 (2H, t, CH_2ArNO_2), 2.40 (4H, t, CH_2CONH), 2.25 (8H, t, $CH_2C{\equiv}C$), 1.75 (4H, quintet, CH_2CCONH), 1.55 (8H, quintet, $CH_2CC{\equiv}C$), 1.30 (44H, m, CH_2), 0.85 (6H, t, CH_3). Anal. Calcd: C, 75.27; H, 9.11; N, 5.76. Found: C, 75.41; H, 9.26; N, 5.78.

Results and Discussion

CV Results. The cyclic voltammograms for solutions of the model compound methyl *N,N*-dimethyl(4-aminophenyl)carbamate (DMAP-C-Me, **24**) and of 4-MTDYAP-C-ENP (**1a**) were measured using a BAS CV-27 potentiostat, with a Pt disc working electrode and a Pt wire counter electrode.[36,37] Table 1 shows that the solution oxidation potential in model donor **24** is unchanged in the diyne **1a**, i.e., the presence of the electron acceptor end A across the σ bridge does not affect greatly the molecular orbitals of the donor end D. Similar findings have been obtained for other non-diyne-containing D–σ–A compounds.[20]

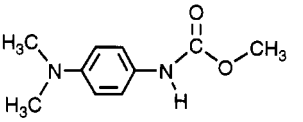
Table 1. Solution Cyclic Voltammetric Potentials[36,37] (All Data Obtained at a Pt Disk Electrode and Given in volts vs SCE)

	oxid (1) D → D+		red. (1) A → A-	
molecule	E_p	$E_{1/2}$	E_p	$E_{1/2}$
model donor: DMAP-C-Me (**24**)[36,a]	0.58	0.55		
D–σ–A: 4-MTDYAP-C-ENP (**1a**)[37,b]	0.57	0.54	−1.09	−1.06

[a] Solvent: CH_3CN. Reference electrode: SCE. A peak at 0.37 V (return scan) grew with successive cycles, indicative of dimer or polymer formation.[36] [b] Solvent: CH_2ClCH_2Cl. Reference electrode: Ag|AgCl. An offset correction of 0.15 V has been applied to convert the values to V vs SCE.

Table 2. Colors Obtained after Exposure to UV Light

compound	color
5	purple-blue
6	light purple
10a	purple
10b	salmon pink
4-MTDYAP-C-ENP, **1a**	purple-blue
3,5-BOTDYAP-C-ENP, **1d**	yellow-orange
3,4-BOTDYAP-C-ENP, **1f**	purple-pink



DMAP-C-Me (**24**)

Polymerization. Solutions of diyne products were spotted on filter paper, and these were placed for several hours under UV light to obtain an indication of their polymerizability. As shown in Table 2, the 3,5-bisamide carbamate **1d** was the least promising D–σ–A compound (orange); **1a** and the 3,4-bisamide isomer **1f** polymerized better (purple).[25]

Monolayer Film Technique. Pockels–Langmuir (insoluble self-assembling monolayer) films[5] were obtained at the air–water interface at room temperature (or below), by using a film balance or Langmuir trough (Lauda) with the water subphase purified to a resistivity of 18 MW cm and made pyrogen-free (Millipore Milli-Q Z040), in a room provided with air filtered by a HEPA (high-efficiency particulate analysis) filter. The subphase was cooled or heated using a recirculating unit (Lauda RM-6 variable-temperature bath) connected to cooling coils mounted below the film balance. Further details are provided elsewhere.[6] For work on **1d** and **1f**, whose diacetylene-containing "tails" were light-sensitive, work was done using illumination from a red safelight in the film balance room. For vertical (Langmuir–Blodgett) transfer onto glass substrates, a Joyce-Loebl film lift was used; the subphase was cooled in some cases to aid in film transfer.

(36) Laidlaw, R. K.; Miura, Y.; Grant, J. L.; Cooray, L.; Clark, M.; Kispert, L. D.; Metzger, R. M. *J. Chem. Phys.* **1987**, *87*, 4967–4971.
(37) Takassi, M. A. Ph.D. Dissertation, University of Mississippi, 1989.

Table 3. Pressure–Area Isotherm Data for Pockels–Langmuir Films

molecule	acceptor type	T, K	Π_t, mN/m	A_t, Å^2	Π_c, mN/m	A_c, Å^2	ref
4-MTDYAP-C-ENP (1a)	weak	278			16.5	63 ± 1	17
3,5-BOHDAP-C-ENP (1c)	weak	299	15.4	83	49.6	39 ± 2	19
		289	15.3	96		45	
		286	15.3	129		47	
		281	16.5	126		47	
3,5-BOTDYAP-C-ENP (1d)	weak	298	19	64	18.7	58 ± 2	19
3,4-BOHDAP-C-ENP (1e)	weak	300	16.3	70	54.5	36 ± 0.5	19
3,4-BOTDYAP-C-ENP (1f)	weak	300	15.8	69 ± 1	49.4	50 ± 1	19
3,4-BOHDAP-C-HETCNQ (1g)	strong	300			55.2	51 ± 1	19

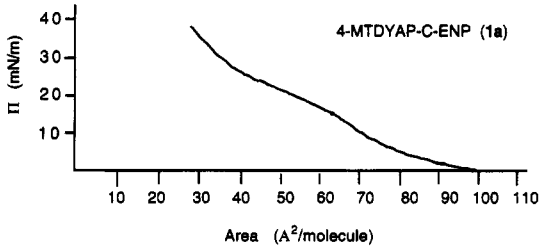


Figure 9. Pressure–area (Π–A) isotherm of 4-MTDYAP-C-ENP (1a) at 278 K.[17]

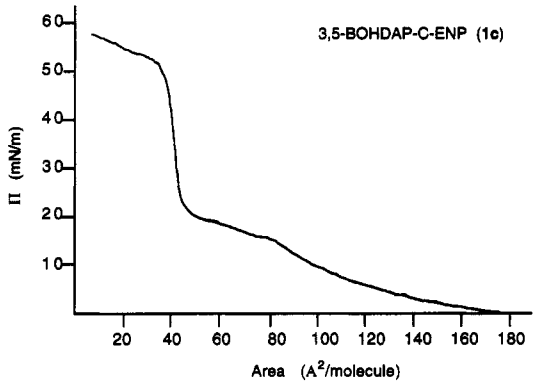


Figure 10. Pressure–area (Π–A) isotherm of 3,5-BOHDAP-C-ENP (1c) at 299 K.

Pockels–Langmuir Film Results. The pressure–area isotherms for molecules **1a** and **1c–g** are given in Figures 9–11, 13–15, and 17–18. (The bisdiyne **1b** was chemically unstable and therefore was not evaluated.) The temperature dependences of the measured molecular areas at collapse (A_c, measured at the film collapse pressure Π_c) for **1c** and **1e** are given in Figures 12 and 16. The pressure and molecular area data are summarized in Table 3. For some of the molecules studied here, a knee was observed in the Π–A isotherm: the pressure Π_t and area A_t at this transition point are also recorded in Table 3. This knee may separate a liquid-expanded phase from a second, liquid-condensed phase.

The first diacetylene-containing molecule synthesized, 4-MTDYAP-C-ENP (**1a**) formed a stable monolayer only at 5 °C (Figure 9); this isotherm had a very low slope $d\Pi/dA$, a low film collapse pressure Π_c, and a molecular area A_c that was only roughly within the range 40–50 Å^2 molecule^{-1} which is expected for these molecules, when packed so that the long molecular axis is perpendicular to the subphase surface.

The model molecule 3,5-BOHDAP-C-ENP (**1c**) was studied as a function of temperature (Figures 10–12). At all temperatures there were two transitions, at Π_t and Π_c. The collapse pressure at 26 °C was respectably large (49.6 mN/m) with molecular areas between 47 Å^2 (at 8 °C) and 39 Å^2 (at 26 °C).

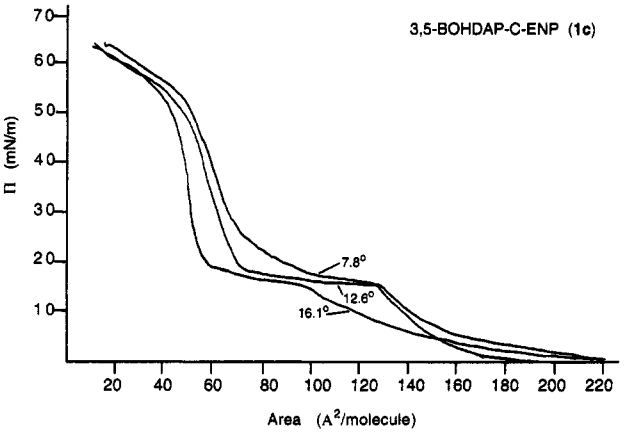


Figure 11. Temperature dependence of the Π-A isotherm of 3,5-BOHDAP-C-ENP (1c).

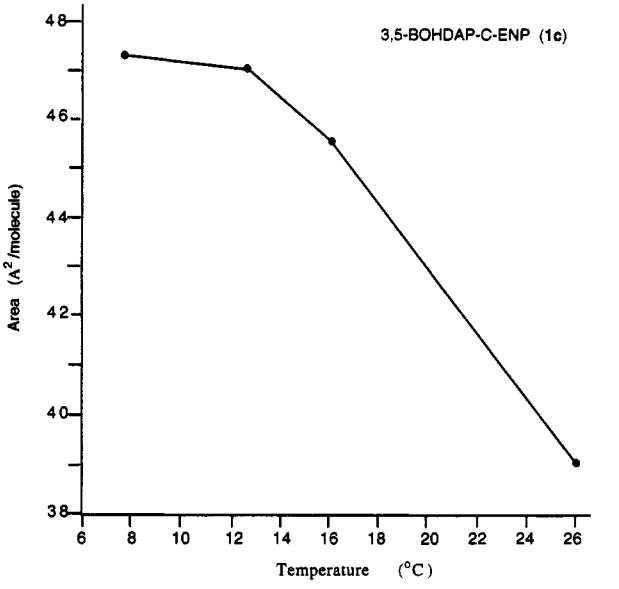


Figure 12. Temperature dependence of the molecular area at film collapse, A_c, of 3,5-BOHDAP-C-ENP (1c).

The diacetylene 3,5-BOTDYAP-C-ENP (**1d**) had the same "knee" as **1c** at relatively low pressure, but no further ordering at higher pressures and lower areas (Figure 13).

The other model molecule, 3,4-BOHDAP-C-ENP (**1e**), also exhibited a "knee" at low pressures and large areas, but also had a relatively steep Π–A curve at lower areas, with a large collapse pressure and molecular areas between 47 Å^2 (at 7–10 °C) and 29 Å^2 (at 35 °C; Figures 14–16).

The diacetylene 3,4-BOTDYAP-C-ENP (**1f**) had a very small "knee" at low pressures, which was quickly followed at lower areas by a steep rise in pressure, and an almost vertical Π–A curve, that ended with a large collapse pressure of 49.4 mN/m, and a molecular area at collapse of 50 Å^2 (Figure 17).

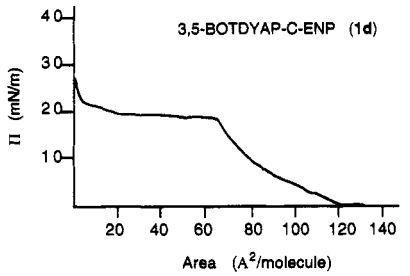


Figure 13. Pressure–area (Π–*A*) isotherm of 3,5-BOTDYAP-C-ENP (**1d**) at 298 K.

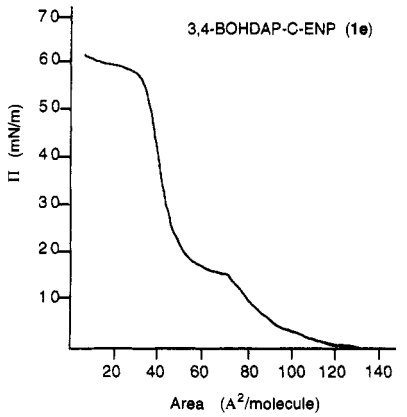


Figure 14. Pressure–area (Π–*A*) isotherm of 3,4-BOHDAP-C-ENP (**1e**) at 300 K.

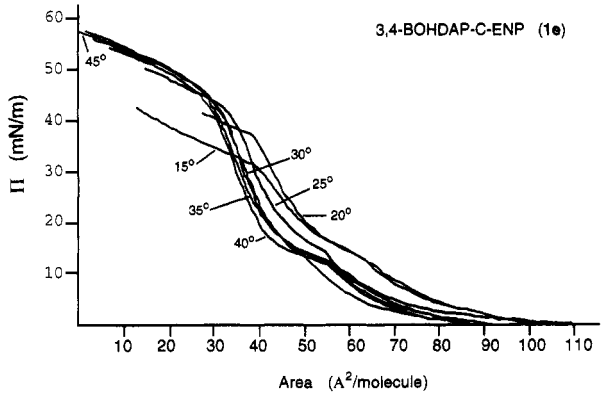


Figure 15. Temperature dependence of the Π–*A* isotherm of 3,4-BOHDAP-C-ENP (**1e**).

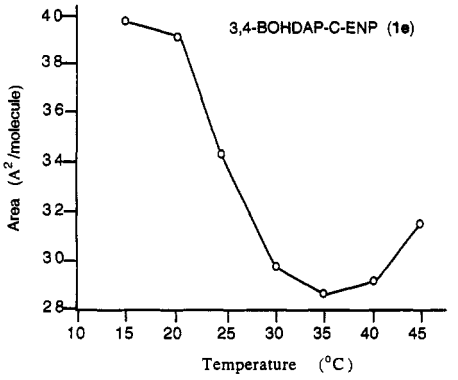


Figure 16. Temperature dependence of the molecular area at film collapse, A_c, of 3,4-BOHDAP-C-ENP (**1e**).

The only molecule in this series that contained the strong electron acceptor TCNQ was 3,4-BOHDAP-C-HETCNQ (**1g**) which had an uneventful Π–*A* isotherm, but, again, an almost vertical Π–*A* curve in the pressure region 30–50 mN/m, approaching the behavior of a solid film, with a collapse pressure of 55.2 mN/m and a molecular area at collapse of 51 Å^2 molecule^{-1}.

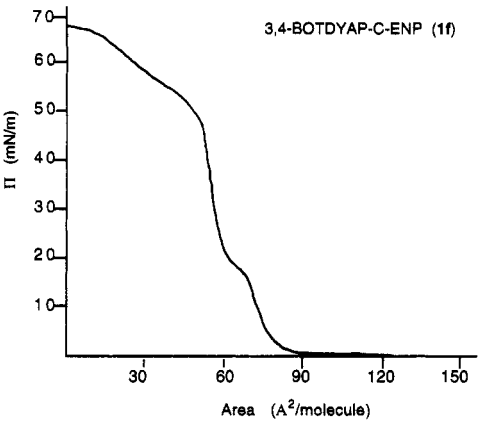


Figure 17. Pressure–area (Π–*A*) isotherm of 3,4-BOTDYAP-C-ENP (**1f**) at 300 K.

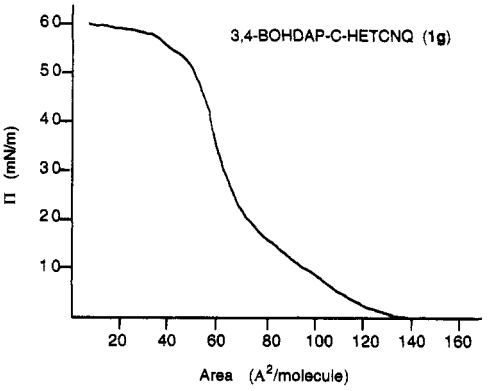


Figure 18. Pressure–area (Π–*A*) isotherm of 3,4-BOHDAP-C-HETCNQ (**1g**) at 300 K.

As judged by the molecular area at collapse, the D–σ–A compound with a single diyne tail, **1a**, gave the least compact film (A_c = 63 Å^2 at 5 °C). Two diyne tails improved the film somewhat; the 3,4 isomer **1f** (A_c = 50 Å^2 at 27 °C) was better than the 3,5 isomer **1d** (A_c = 58 Å^2 at 25 °C and a very low collapse pressure). The most compact monolayers were those of the saturated-tailed molecules: the 3,4 isomer (**1e**, A_c = 34 Å^2 at 25 °C) again displayed closer packing than the 3,5 isomer (**1c**, A_c = 39 Å^2 at 26 °C).

Langmuir–Blodgett Film Results. For both of the bis(saturated amide) compounds 3,5-BOHDAP-C-ENP (**1c**) and 3,4-BOHDAP-C-ENP (**1e**) there were serious problems in making LB films at room temperature: the transfer ratio for the first monolayer for either molecule was zero; decreasing the subphase temperature to 7.4 °C (bath temperature 5 °C) did not improve the transfer.

In contrast, multilayers of 3,4-BOTDYAP-C-ENP (**1f**) transferred very regularly and evenly to an aluminum-coated glass substrate, except that the first monolayer had a relatively low (but not zero) transfer ratio. When held under a UV lamp for 24 h, a multilayer LB film of **1f** turned pale blue. By visual inspection, the film was fairly transparent. As a second alternative for making multilayers of **1f**, the Pockels–Langmuir monolayer was first polymerized with UV light at the air–water interface. The transfer of the prepolymerized **1f** was, once again, poor for the first layer, then intermediate for the second, fourth, sixth, etc. layers, but good for layers three, five, seven, etc.

Table 4. Third-Order Nonlinear Optical Susceptibility $\chi^{(3)}$ of D–σ–A Molecules in Chloroform Solution at Room Temperature, Using an Ar^+ Laser at 514.5 nm, as Quoted in Ref 19

molecule	P_c, mW	$\chi^{(3)}$, esu
3,5-BOHDAP-C-ENP (1c)	200	6.8×10^{-8}
3,4-BOHDAP-C-ENP (1e)	130	1.1×10^{-7}
3,4-BOHDAP-C-HETCNQ (1g)	130	2.5×10^{-6}

No attempts were made to transfer the other bis(diyne amide), 3,5-BOTDYAP-C-ENP (**1d**), onto solid substrates, because of its low collapse pressure.

Nonlinear Optical Results. Third-order nonlinear optical properties were measured for three of the compounds, as given in Table 4. The compounds, dissolved in chloroform, were studied by the technique of laser self-trapping: continuous-wave beam from an argon ion laser (λ = 514.5 nm) is focused in the sample solution, while the beam diameter is monitored visually at a fixed distance. At a critical power P_c for self-trapping, the beam diameter just starts to shrink. The third-order nonlinear electrical susceptibility $\chi^{(3)}$ is then given by $0.00125nc\lambda^2/P_c$ in units of esu, where c is the speed of light, n is the linear refractive index, and λ = 514.5 nm. For comparison, $\chi^{(3)} = 10^{-12}$ esu for liquid CS_2. The data in Table 4 are dramatic but should not be taken at face value. It is quite likely that these self-trapping measurements have measured not the pure nonresonant third-order nonlinear optical coefficient, but a nonlinearity which probably includes the effects of resonance, optical absorption in the visible region (in the case of **1g**) and localized heating of the solution. Fast (10^{-9} s) measurements of $\chi^{(3)}$ by degenerate four-wave mixing can yield values of nonresonant $\chi^{(3)}$ 3 or more orders of magnitude smaller than the self-trapping values.[38] The $\chi^{(3)}$ values are useful, however, as an indication of nonlinear optical activity.

Conclusion

The synthetic goal of coupling D–σ–A molecules with diacetylenes has been accomplished. One of these molecules, **1g**, has the strong acceptor TCNQ incorporated into it, makes strong films with a large collapse pressure, and has significant third-order nonlinear optical activity. Lipid tail attachment at the 3 and 4 positions of a donor benzene ring (**1e**, **1f**) afforded better film characteristics than 3,5-disubstituted isomers (**1c**, **1d**); two diyne tails at the 4 position gave a chemically unstable compound (**1b**) unsuitable for film studies. The polymerizations of monodiyne **1a** and bisdiyne **1f** seem to yield the best conditions for topotactic polymerization; **1f** gave polymerizable LB multilayers. It appears that the class of compounds presented here should afford interesting future results, both as polymerizable diacetylenes and as nonlinear optical films.

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(38) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.