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13. ABSTRACT (Maximum 200 words)  
The synthetic chemistry of dithiadiazafulvalenes (DTDAF) was studied in detail: these one and two-electron donors, ore powerful than the well-known tetrathiafulvalenes (TTF, 1), but more chemically more tractable than the unstable tetraazafulvalenes, are a significant departure from ordinary organic donors, and therefore show promise in the search for new organic superconductors. A 2:5 complex of diphenyl-diacetyldithiadiazafulvalene (o2Ac2DTDAF, 4c) with the electron acceptor tetracyanoquinodimethan (TCNQ, 11a), including one molecule of acetonitrile, the solvent of crystallization (CH3CN), provided room-temperature conductivity  $\sigma=0.011$  S/cm (Siemens per centimeter). An unusual diamagnetic flux exclusion signal (for 5 per cent of the sample at 4.4 Kelvin) was determined to be an artifact due to a ferromagnetic impurity. A TCNQ complex of dimethyltetracetylDTDAF, 4b had  $\sigma=0.083$  S/cm at room temperature. A new acceptor, dioxotetracyanobisindanedione vinylidene (DOTCBIV), 5, provided a complex with TTF with  $\sigma=0.6$  S/cm at room temperature. Many complexes wity fullerene, C60 (12), were made, but were electrically insulating. Studies of Langmuir-Blodgett films of potassium-doped C60 (monolayers on polyethylene terephthalate) may help to determine the boundary between 2-D and 3-D superconductivity.

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February 12, 1997

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Dear Drs. Weinstock and Lee:

Enclosed please find nine copies (sent to Dr. Lee) plus one copy (to Dr. Weinstock) of the Final Report for AFOSR Contract F-49620-92-J-0529 (Organic and Polymeric Superconductors). Thank you very much for your past support.

Robert M. Metzger  
Professor

cc: Dr. Robert Wells, Assistant Vice President for Research  
Pam Standifer, Contracts and Grants Accounting

## Final Report to Air Force Office of Scientific Research

Date: February 12, 1997

Period 1 October 1992 - 1 March 1996

Grant Title: Organic and Polymeric Superconductors

AFOSR Grant No. F-49620-92-J-0529

Principal Investigator: Robert M. Metzger

Co-Investigator: Michael P. Cava

Institution: Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487-0336

Cognizant AFOSR Program Managers: Charles Y.C. Lee and Harold Weinstock

### Abstract

The synthetic chemistry of dithiadiazafulvalenes (DTDAF) was studied in detail: these one and two-electron donors, more powerful than the well-known tetrathiafulvalenes (TTF, **1**), but more chemically more tractable than the unstable tetraazafulvalenes, are a significant departure from ordinary organic donors, and therefore show promise in the search for new organic superconductors. A 2:5 complex of diphenyldiacetyldithiadiazafulvalene ( $\phi_2\text{Ac}_2\text{DTDAF}$ , **4c**) with the electron acceptor tetracyanoquinodimethan (TCNQ, **11a**), including one molecule of acetonitrile, the solvent of crystallization ( $\text{CH}_3\text{CN}$ ), provided room-temperature conductivity  $\sigma=0.011$  S/cm (Siemens per centimeter). An unusual diamagnetic flux exclusion signal (for 5 per cent of the sample at 4.4 Kelvin) was determined to be an artifact due to a ferromagnetic impurity.

A TCNQ complex of dimethyltetracetylDTDAF, **4b** had  $\sigma=0.083$  S/cm at room temperature. A new acceptor, dioxotetracyanobisindanedione vinylidene (DOTCBIV), **5**, provided a complex with TTF with  $\sigma=0.6$  S/cm at room temperature. Many complexes with fullerene,  $\text{C}_{60}$  (**12**), were made, but were electrically insulating.

Studies of Langmuir-Blodgett films of potassium-doped  $\text{C}_{60}$  (monolayers on polyethylene terephthalate) may help to determine the boundary between 2-D and 3-D superconductivity.

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### 1. Dithiadiazafulvalenes - New Strong Electron Donors.

As a novel variation on tetrathiafulvalene (TTF) **1**, its selenium and tellurium analogs, and their derivatives, we prepared new donors (dithiadiazafulvalenes, DTDAFs) **4a**, **4b**, **4c**, and **4d**; their electrochemistry (Table I) shows them to be powerful new donors.

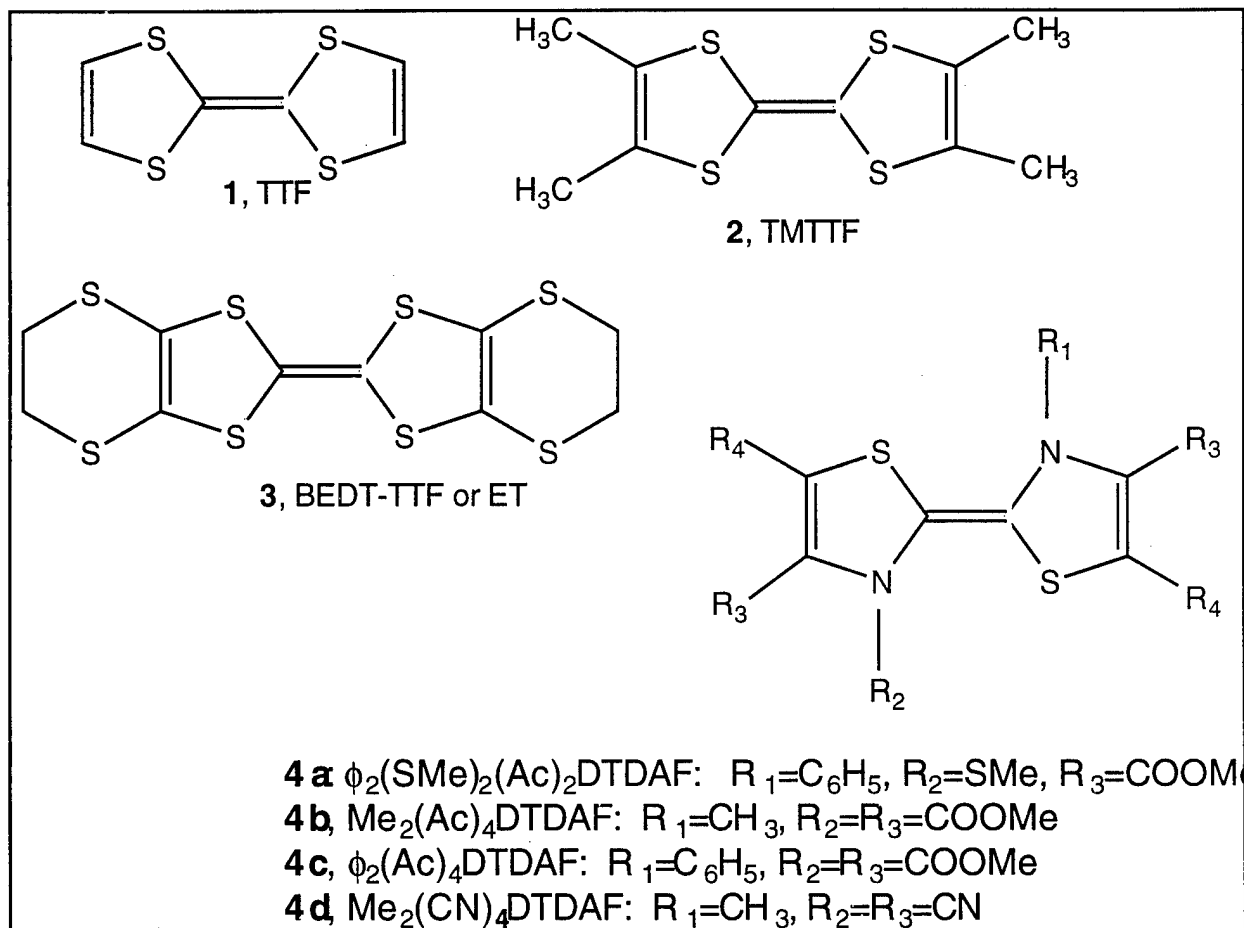


Table I. Oxidation potentials of TTF (1), TMTTF (2), and BEDT TTF (3) and of the novel DTDAFs **4a**, **4b**, **4c**, and **4d**, determined by cyclic voltammetry (V vs. SCE).

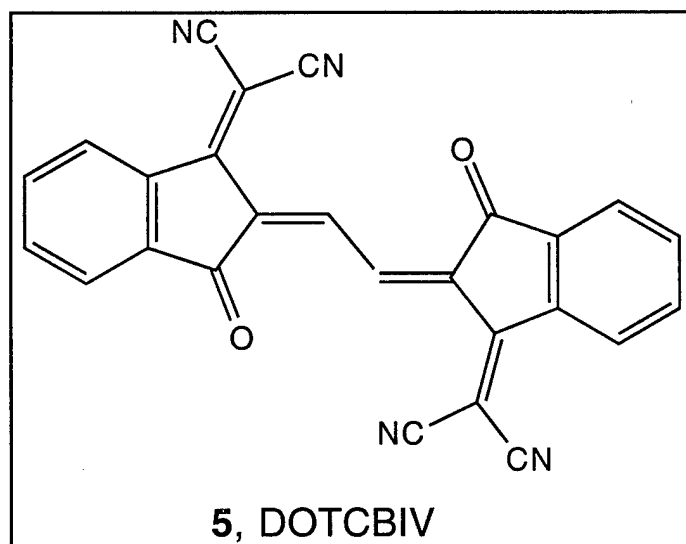
Compound	$E^1_{ox}$ , V	$E^2_{ox}$ , V	$E^2_{ox} - E^1_{ox}$ , V
TTF (1)	0.35 [13]	0.71 [13]	0.36 [13]
TMTTF (2)	0.29 [13]	0.65 [13]	0.36 [13]
ET (3)	0.58	1.00	0.42
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$ , <b>4a</b>	0.00	0.48	0.48
$\text{Me}_2\text{Ac}_4\text{DTDAF}$ <b>4b</b>	0.02	0.26	0.24
$\phi_2\text{Ac}_4\text{DTDAF}$ , <b>4c</b>	0.15	0.66	0.51
$\text{Me}_2(\text{CN})_4\text{DTDAF}$ , <b>4d</b>	0.42	0.63	0.21

In complexes with the electron acceptor TCNQ, they yielded new semiconductors (Table 2) but no new metals.

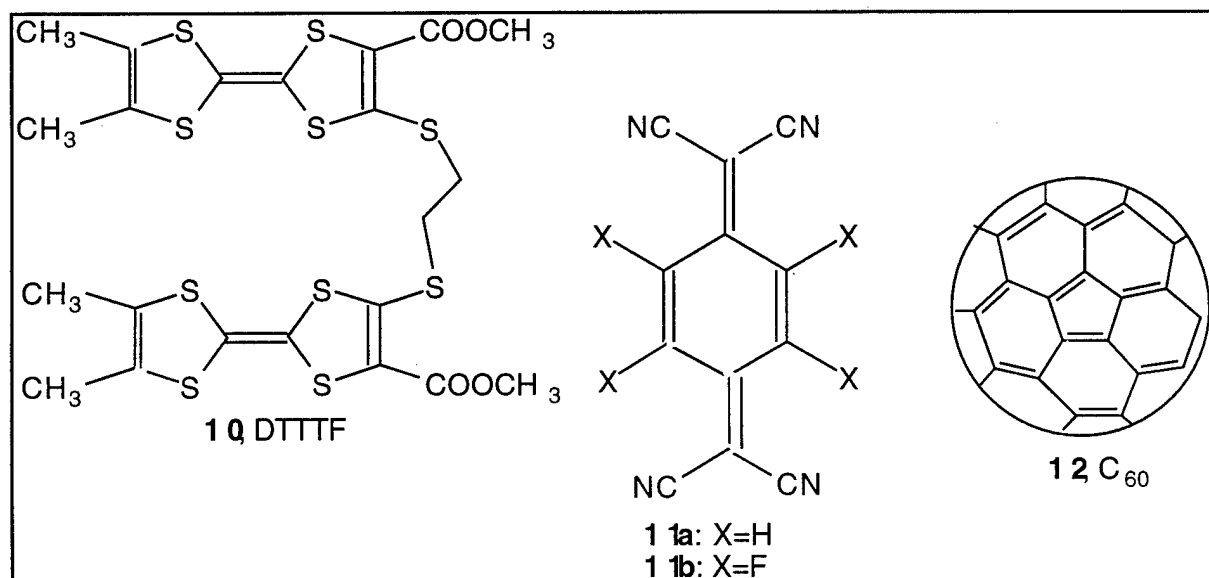
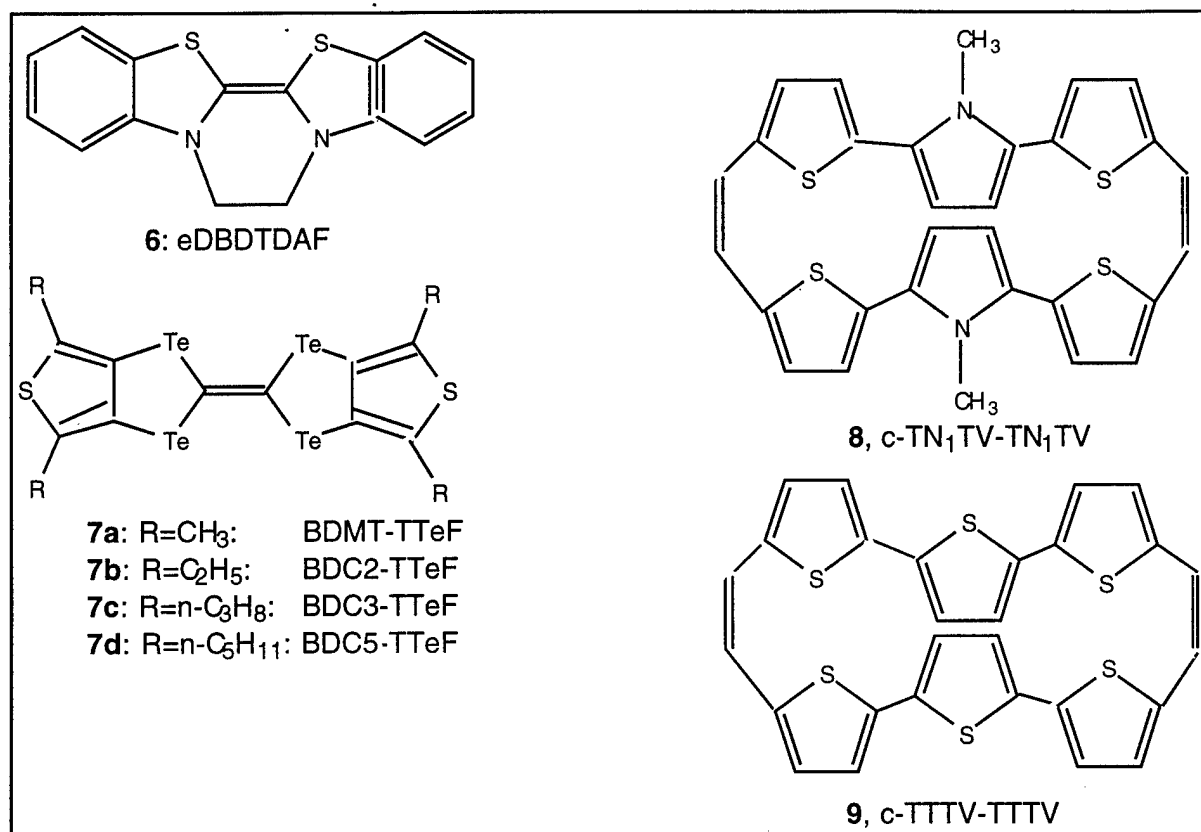
Table 2. Room temperature conductivities of complexes of **4a**, **4b**, **c** with TCNQ (standard 2-probe method, compaction, gold wire, gold paste).

Donor	Acceptor	Ratio	Conductivity (300 K) $\sigma$ , $\text{S cm}^{-1}$
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$ , <b>4a</b>	TCNQ	1:1	$1.6 \times 10^{-7}$
$\phi_2(\text{SMe})_2\text{Ac}_2\text{DTDAF}$ , <b>4a</b>	TCNQ	1:4 (+ 2 $\text{CH}_3\text{CN}$ )	$1.1 \times 10^{-7}$
$\text{Me}_2\text{Ac}_4\text{DTDAF}$ <b>4b</b>	TCNQ	1:4	$8.3 \times 10^{-2}$
$\phi_2\text{Ac}_4\text{DTDAF}$ , <b>4c</b>	TCNQ	1:1	$10^{-10}$
$\phi_2\text{Ac}_4\text{DTDAF}$ , <b>4c</b>	TCNQ	2:5	$1.1 \times 10^{-2}$

## 2. New Electron Acceptor



A new one-electron acceptor, dioxotetracyanobisindanedione vinylidene DOTCBIV, **5** is a strong electron acceptor, with two quasi-reversible electrochemical reduction waves ( $E^1_{red} = 0.05$ ,  $E^2_{red} = -0.11$ ;  $E^1_{ox} = -0.06$ ,  $E^2_{ox} = 0.11\text{V}$  vs SCE, in acetonitrile). It reacts with TTF and TMTTF to form charge-transfer complexes, whose room-temperature conductivities (2-probe method, compaction, gold wire, gold paste) are 1.7 and 0.01 S/cm respectively. An effort to prepare the octacyano derivative of BIV was not successful.



### 3. Physical Measurements.

The Langmuir-Blodgett films of C<sub>60</sub> [1,2] form monolayers only from very dilute dropping solutions (0.05 mg/mL), and then give areas of about 96 Å<sup>2</sup>/molecule, i.e. a true monolayer forms [3]. When doped with K, a 50 monolayer sample of C<sub>60</sub> shows a low-field signal, measured in an EPR spectrometer, with hysteresis, at or below 8.1 K: this is a sensitive test of the Meissner effect for some unknown fraction of the sample, due to the formation of K<sub>3</sub>C<sub>60</sub> within the LB multilayer: **the world's first superconducting Langmuir-Blodgett film** [4-

6]. When more K is added, the signal disappears (formation of insulating  $K_6C_{60}$ ) [4,5]. A new study of the superconductivity of  $K_3C_{60}$  LB films finds slightly higher critical temperatures [13].

The physical results for many of the complexes described in Table 3 have been published [6-9]. Overall, three are promising conductors:  $(4b)_2(TCNQ)_5CH_3CN$ ,  $4a+TCNQ$ ,  $1+25a$ . The crystal structure of the 1:5 complex of **7** with **32a** has been determined by Robert and co-workers: the neutral and anionic TCNQ species form a segregated stack, while the DTDAF cations do not overlap with each other: this is a classic "mixed" TCNQ stack structure, with expected semiconductive properties. By crystal structure analysis,  $(4b)_2(TCNQ)_5CH_3CN$  forms a similar structure, with good TCNQ stacks, but where the phenyl rings on DTDAF **4b** prevent efficient stacking of the DTDAF moieties.

Table 3. List of complexes and their conductivities.

Donor	Acceptor	Solvent	Stoich.	Size, mm	Phys. Properties
$\phi_2(SMe)_2Ac_2DTDAF$ , <b>4a</b>	TCNQ, <b>11a</b>	CH <sub>3</sub> CN	1:1	powder	black $\sigma=1.6 \times 10^{-7}$ S/cm
	TCNQ, <b>11a</b>	CH <sub>3</sub> CN	1:4+2	CH <sub>3</sub> CN	black powder $\sigma=1.12 \times 10^{-7}$ S/cm
Me <sub>2</sub> Ac <sub>4</sub> DTDAF, <b>4b</b>	TCNQ, <b>11a</b>	CH <sub>3</sub> CN	1:4	powder	black powder $\sigma=8.3 \times 10^{-2}$ S/cm
$\phi_2Ac_4DTDAF$ , <b>4c</b>	TCNQ, <b>11a</b>	(CH <sub>2</sub> Cl) <sub>2</sub> +CH <sub>3</sub> CN	2:5	1.0×0.4×0.07	black plate, $\sigma=0.011$ S/cm [9]
		CH <sub>2</sub> Cl <sub>2</sub>	1:1	1.1×1.0×0.1	black plate, $\sigma < 10^{-10}$ S/cm [9], polycrystalline
		CH <sub>3</sub> CN	1:2	small	black tiny plate
	TCNQF <sub>4</sub> , <b>11b</b>	C <sub>6</sub> H <sub>5</sub> Cl+CH <sub>2</sub> Cl <sub>2</sub>	1:x	1.6×1.1×0.01	black polycryst. [9] plate $\sigma=1.2 \times 10^{-6}$ S/cm
		C <sub>60</sub> , <b>12</b>	CH <sub>2</sub> Cl <sub>2</sub> +CS <sub>2</sub>	1:x	1.5×0.04×0.03
	I <sub>2</sub>	CHCl <sub>3</sub>	1:x	0.8×0.7×0.6	black $\sigma=1.1 \times 10^{-7}$ S/cm OK for X-ray [9]
			C <sub>2</sub> H <sub>5</sub> OC <sub>2</sub> H <sub>5</sub>	1:x	0.5×0.04×0.04
eDBDTDAF, <b>6</b>	TCNQ, <b>11a</b>		2:1	powder	black, $\sigma < 10^{-10}$ S/cm
TTF, <b>1</b>	DOTCBIV, <b>5</b>	CH <sub>2</sub> Cl <sub>2</sub> +n-C <sub>6</sub> H <sub>14</sub>	1:x	powder	$\sigma=0.6$ S/cm
BDMT-TTeF, <b>7a</b>	DOTCBIV, <b>5</b>	CH <sub>2</sub> ClCH <sub>2</sub> Cl+CS <sub>2</sub>	1:x	needle	black, $\sigma < 10^{-10}$ S/cm
BDMT-TTeF, <b>7a</b>	TCNQ, <b>11a</b>	CH <sub>2</sub> ClCH <sub>2</sub> Cl	1:x		tiny plate
		C <sub>60</sub> , <b>12</b>	1:x		tiny plate.
	C <sub>60</sub> , <b>12</b>	CS <sub>2</sub>	1:1+1	CS <sub>2</sub>	rhombic plate, cryst.str. [6] $\sigma < 10^{-10}$ S/cm [7]
		CS <sub>2</sub>	1:x		hexagonal plate
BD2T-TTeF, <b>7b</b>	C <sub>60</sub> , <b>12</b>	CH <sub>2</sub> Cl <sub>2</sub> +CS <sub>2</sub>	1:x	1.0×0.9×0.04	black polycrystal, $\sigma < 10^{-10}$ S/cm
BD3T-TTeF, <b>7c</b>	C <sub>60</sub> , <b>12</b>	CS <sub>2</sub>	1:x	0.8×0.7×0.02	$\sigma < 10^{-10}$ S/cm
BD5T-TTeF, <b>7d</b>	C <sub>60</sub> , <b>12</b>	CS <sub>2</sub>	1:x	0.4×0.3×0.02	$\sigma < 10^{-10}$ S/cm
DTTF, <b>10</b>	C <sub>60</sub> , <b>12</b>	CS <sub>2</sub> or C <sub>6</sub> H <sub>6</sub>	1:x	1.5×0.05×0.04	needle, insulator [9]
c-TTTV-TTTV, <b>8</b>	TCNQF <sub>4</sub> , <b>11b</b>		1:1	powder	$\sigma=9.5 \times 10^{-3}$ S/cm [8]
c-TN <sub>1</sub> TV-TN <sub>1</sub> TV, <b>9</b>	TCNQF <sub>4</sub> , <b>11b</b>		1:1	powder	$\sigma=1.2 \times 10^{-4}$ S/cm [8]

The synthetic chemistry of the dithiadiazafulvalenes has been published in full [10]. The criteria for the formation of organic superconductors, and of the limiting conductivity of organic polymers has been published [11]. A new polymeric semiconductor has also been studied [12].

#### 4. References credited to this Contract.

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Dr. Gregory V. Tormos (present employment: Eastman Chemical Co., Batesville, AR)

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None.