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Synthesis of Monomers and Polymers and Charge-Transfer Complexes Containing the Electron Donating 2-Arylidene-1,3-dithiole Unit

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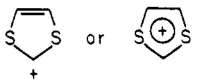
ABSTRACT: Model compounds, 2-benzylidene-1,3-dithioles (**3**–**6**), and monomers, 2-(*p*-vinylbenzylidene)-1,3-dithioles (**7**–**9**), containing the electron donating 2-arylidenene-1,3-dithiole heterocycle have been prepared. Homopolymers and copolymers of compounds **7** and **8** are described, the best method of homopolymerization being dissolution in concentrated sulfuric acid. Model compounds **1** and **5** were found to form 1:1 charge-transfer complexes with TCNQ. Compound **3** formed a 2:1 TCNQ complex. With trinitrofluorenone, compound **3** and the homopolymer of **7** also formed charge-transfer complexes.

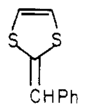
Since the discovery of the exceptional electrical conductivity of the tetrathiafulvalene (TTF)–tetracyanoquinonedimethane complexes (TCNQ), many reports have been published concerning the preparation of donor–acceptor (DA) substances, both low molecular weight and polymeric.[1]

The 1,3-dithiolium ion **1** is an unsaturated five-membered-ring cation in which each sulfur atom can contribute a pair of 3pπ electrons and, consequently, would be expected to exhibit aromatic stability and ease of formation.[2]



1

The 2-benzylidene-1,3-dithioles **2** could also react to form a thiolium cation by protonation at the benzylic carbon atom or by oxidation.

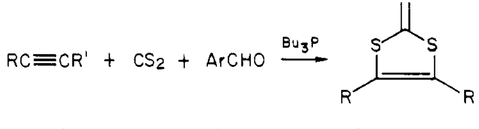


2

In this work, the syntheses of model compounds, monomers, and polymers containing the heterocyclic **2** unit are described. In a previous paper, the syntheses of electron-accepting monomers and polymers containing di- and tricyano groups were reported.[6]

Syntheses

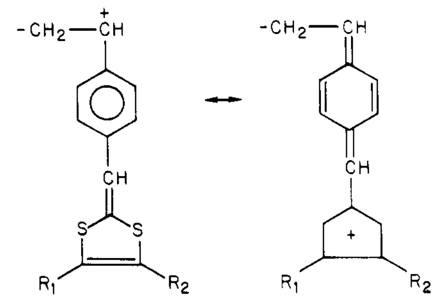
New compounds were synthesized by the method of Hartzler.[3] Acetylenes having at least one electron-withdrawing substituent reacted readily with benzaldehyde or *p*-vinylbenzaldehyde to form easily isolable crystalline dithioles in fair yield. Phenyl acetylene and diphenylacetylene reacted slowly to give dithioles in low yield. Results are reported in Tables I and II.



Compounds **3**, **6**, **8**, and **9** are capable of existing in geometrically isomeric forms. From NMR spectra and the melting point it is possible that **4** and **8** were obtained as single isomers whereas **6** was a cis–trans mixture and **9** is uncertain.

The polymerizability of the vinyl carboalkoxy derivatives **7** and **8** was investigated. Radical polymerization using AIBN in refluxing benzene or THF was unsuccessful in the case of **7** and gave only a low yield of low molecular weight polymer in the case of **8**. There is reason to believe that the dithiole ring may behave as a retarder or inhibitor in radical polymerization because when an equimolar mixture of **7** and styrene was heated in the presence of AIBN no polymerization occurred. However, **3** can be radically copolymerized with methyl methacrylate (MMA), α-methylacrylophenone (α-MAP), and α-chloroacrylonitrile (Cl-AN) to give 1:1 low molecular weight copolymers with low conversion (Table III).

It might be anticipated that carbocations would be readily formed from Lewis acids and **7** or **8** because of stabilization by the dithiole ring as shown below. Unfortunately, the monomers which were available in sufficient quantity to be studied contained one or more electron-withdrawing carboalkoxy groups which would certainly not enhance carbocation formation. In fact, both $SnCl_4$ and BF_3 produced polymer **10** reluctantly (Table III). The best method for polymerization of **7** was found to be dissolution in concentrated sulfuric acid at room temperature which provided an 85% yield of polymer **10** after 4 h having a molecular weight (ebulioscopic) of 7000 ($\overline{DP}_n$ = 20). The composition and spectral data are in accord with structure **10**, including the presence of the dithiole ring. In particular, the NMR spectrum revealed the transformation of the vinyl group to $-CH_2CH<$ and



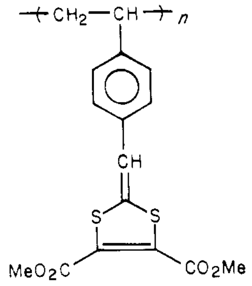


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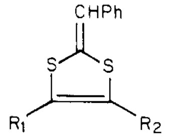
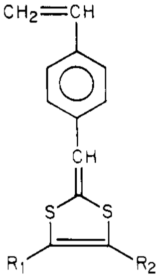
Table I
Syntheses and Properties of 2-Benzylidene-1,3-dithioles



compd no.	R_1	R_2	reaction temp, °C	reaction time, h	color	% yield	mp, °C	solvent, λ_{max} (nm), ϵ	NMR (benzylidene H) chemical shift, solvent (δ)
3	CO_2Me	CO_2Me	−23	0.5	red needles	47	97–98	$CHCl_3$, 328, 16 400	$CDCl_3$ (6.4)
4	H	Ph	25	8	yellow plates	10	204 dec		CS_2 (6.4)
5	Ph	Ph	25	1 week	yellow	5	124	CH_3CN, 339, 21 200	$CDCl_3$ (6.45)
6	H	CO_2Et	−23	1	yellow	30	102–108	EtOH, 340, 17 100	$CDCl_3$ (6.55)

Table II
Syntheses and Properties of 2-(*p*-Vinylbenzylidene)-1,3-dithioles



compd no.	R_1	R_2	reaction temp, °C	reaction time, h	color	% yield	mp, °C	solvent, λ_{max} (nm), ϵ	NMR (benzylidene H) chemical shift, solvent (δ)
7	CO_2Me	CO_2Me	−23	0.5	orange red	57	99.5	EtOH, 345, 24 000	$CDCl_3$ (6.40)
8	H	CO_2Et	−23	1	yellow	57	122–123	EtOH, 363, 28 900	$CDCl_3$ (6.4)
9	H	Ph	25	8	yellow	10	228	CH_2Cl_2, 378, 27 200	CF_3CO_2H

the retention of the benzylidene proton at δ 6.4. In the ultraviolet, polymer **10** showed a red shift relative to monomer **9** with $\lambda_{max}^{CHCl_3}$ 328 nm (ϵ 12 500) which is the same as that for model compound **3**.

In order to prepare polymer **10** by an alternate route with the possibility of obtaining higher molecular weight product, *p*-vinylbenzaldehyde was synthesized and polymerized free radically. The polymer was then treated with dimethyl acetylenedicarboxylate in THF under the same conditions as were described for the monomers or model compounds. Polymer **10** prepared in this manner had $\lambda_{max}^{CHCl_3}$ 326 nm (ϵ 13 000) the same as the polymer produced from monomer **9**. From the sulfur content it was found that 82% of the aldehyde groups had been converted to dithiole.

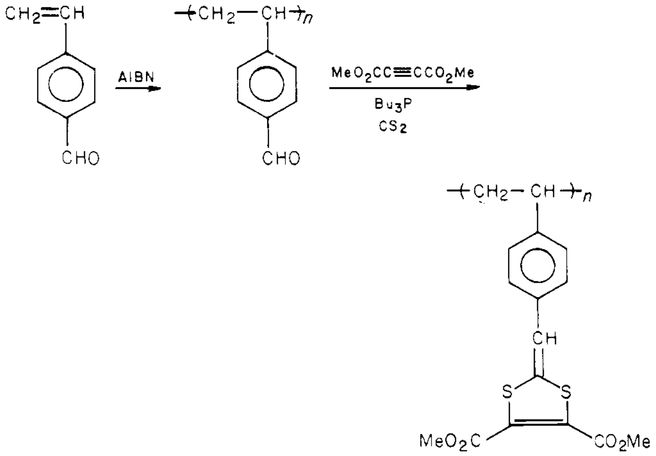
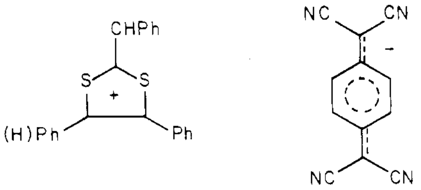


Table III[a]
Copolymerization of Compound 7

comonomer	time, h	conversion, wt %	η_{inh}[b]	mol % of 7 in copolymer
MMA	28	12	0.02	50
α-MAP	43	10	0.01	50
Cl-AN	48	23	0.01	51

[a] Copolymerization conditions: 1 mmol of **7** and 1 mmol of comonomer containing 0.05 mmol of AIBN in 10 mL of benzene were heated under reflux. [b] Inherent viscosities were determined on a 0.5% solution in benzene at 30.0 °C.

Model compounds **4** and **5** readily formed 1:1 charge-transfer complexes with TCNQ in acetonitrile, which are shown in their fully charge separated form below.



Charge-transfer formation was shown by the appearance of C-T bands in the visible region of the spectrum[7] between 600 and 900 nm as well as by NMR and infrared spectroscopy. In particular, the NMR showed the TCNQ protons as an A_2B_2 quartet at δ 7.5–7.9 indicating restricted rotation in the complex.

In contrast, model compound **3**, containing two carbomethoxy groups, formed a complex with TCNQ in acetonitrile containing a 2:1 ratio of dithiole to TCNQ. However, in THF only starting materials were recovered. Unlike the CT complex from the mono- or diphenyl compound, this 2:1 complex showed the TCNQ protons as a singlet at δ 7.8 in the NMR spectrum.

When model compound **3** and trinitrofluorenone (TNF) were allowed to react in hot ethanol, a dark green 1:1 complex separated. The carbonyl bond of TNF had shifted from 1735 to 1700 cm^{-1} in the IR spectrum, but no obvious change in the UV-visible or NMR spectra was observed. This provides evidence that the complex is largely dissociated in solution.

In benzene, polymer **10** reacted with TNF to produce a dark green solid, analysis of which showed that half of the dithiole rings had complexed with TNF.

Further work on the reactions and properties of these substances will be reported.

Experimental Section

Melting points were determined on a Fisher-Johns melting point or a Mel-Temp apparatus and are uncorrected. Nuclear masgnetic resonance (NMR) spectra were determined on a Varian Model T-60 (60 MHz) NMR spectrometer, using tetramethylsilane as a standard. Infrared spectra were determined using either a Perkin-Elmer infracord or a Perkin-Elmer model 337 grating infrared spectrometer and calibrated with a polystyrene film. Ultraviolet, visible, and near infrared absorption spectra were determined using a Cary 14 recording spectrometer. A Varian model E-3 EPR spectrometer was used to determine epr spectra. Viscosities were determined using Ubbelohde type or Cannon-Fenske viscometers. Inherent viscosities (dL/g) were determined in 0.5% solution at 30 °C.

Elemental analyses were determined by Huffman Laboratories, Inc., Wheatridge, Colo.

Dimethyl 2-Benzylidene-1,3-dithiole-4,5-dicarboxylate (3). The preparation of 2-benzylidene-1,3-dithioles, other than the ones reported here, has appeared in the literature,[3] but experimental details were not described.

Dimethyl acetylenedicarboxylate (7.0 g, 0.049 mol) was added during 10 min to a solution of 10.0 g (0.049 mol) of tri-*n*-butylphosphine, 3.7 g (0.049 mol) of carbon disulfide, and 5.2 g (0.049 mol) of benzaldehyde in 14 mL of diethyl ether at -23 °C under nitrogen. A red-orange solid, 7.2 g (48%), precipitated from solution. Recrystallization from ethanol gave red-orange needles: mp 97–98 °C; IR (KBr) 1740, 1720, 1590, 1550, 1500, 1440, 1350, 1240, 1100, 1020, 1000, 930, 850, 820, 780, 760, 755, and 690 cm^{-1}; NMR (CDCl$_3$) δ 7.2 (mult, 5 H), δ 6.4 (s, 1 H), and δ 3.8 (s, 6 H); UV $\lambda_{max}^{CHCl_3}$ 410 nm (ε 1600), 328 (ε = 16400), and 245 (ε = 14000).

Anal. Calcd for $C_{14}H_{12}O_4S_2$: C, 54.5; H, 3.9; S, 20.8. Found: C, 54.5; H, 4.02; S, 21.2.

Dimethyl 2-(*p*-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate (7). *p*-Vinylbenzaldehyde (1.32 g, 0.010 mmol) was added to the purple-red complex of carbon disulfide (0.76 g, 0.010 mmol) and tri-*n*-butylphosphine (2.02 g, 0.010 mmol) in 10 mL of absolute ether. Dimethyl acetylenedicarboxylate (0.010 mmol, 1.42 g) in 5 mL of absolute ether was then added dropwise over 10 min. At the end of the addition, a red precipitate formed suddenly, and the mixture was stirred 10 min more. After filtration and crystallization of the precipitate from 20 mL of hot 95% ethanol, 1.59 g of orange-red needles (57%) were obtained: mp 99.5 °C; mass spectrum, *m/e* 334; IR (KBr) 1725 (s), 1580 (s), 1435, 1250 (s), 1100, 1030, 995, 920 cm^{-1}; NMR (CDCl$_3$) δ 3.80 (s, 6 H), 5.25 (q, 1 H), 5.80 (q, 1 H), 6.40 (s, 1 H), 6.45–6.95 (q, 1 H), 7.05–7.50 (q, 4 H); UV λ_{max}^{EtOH} 410 nm (500), 359 (sh) (22700), 345 (24000), 245 (17500).

Anal. Calcd for $C_{16}H_{14}S_2O_4$: C, 57.50; H, 4.19; S, 19.15. Found: C, 57.60; H, 4.23; S, 19.06.

Ethyl 2-(*p*-Vinylbenzylidene)-1,3-dithiole-4-carboxylate (8). *p*-Vinylbenzaldehyde (2.64 g, 20 mmol) was added to a complex of carbon disulfide (1.52 g, 20 mmol) and tri-*n*-butylphosphine (4.04 g, 20 mmol) under nitrogen at -23 °C in a carbon tetrachloride dry ice bath. Ethyl propiolate (1.96 g, 20 mmol) in 15 mol of absolute ether was then added through an addition funnel over 10 min and the solution was stirred 10 min more at -23 °C. While still cold, the reaction mixture was filtered through sintered glass and 2.46 g of yellow crude product was obtained (57% yield). After crystallization from 200 mL of ether at -20 °C, yellow plates were obtained: mp 122–123 °C; IR (KBr) 1700 (s), 1580, 1410 (w), 1300, 1210, 1070 (s), 920, 860 (s), 735 (s) cm^{-1}; NMR (CDCl$_3$) δ 1.3 (t, 3 H), 4.3 (q, 2 H), 5.2 (q, 1 H), 5.7 (q, 1 H), 6.4 (s, 1 H), 6.5–6.9 (q, 1 H), 7.2 (5 H); mass spectrum, *m/e* 290; UV λ_{max}^{EtOH} 405 nm (sh) (3500), 363 (28900), 355 (sh) (28000), 246 (18250).

Anal. Calcd for $C_{15}H_{14}S_2O_2$: C, 62.10; H, 4.86; S, 22.08. Found: C, 61.71; H, 4.83; S, 22.54.

Ethyl 2-Benzylidene-1,3-dithiole-4-carboxylate (6). The procedure is the same as above. The compound was obtained in 30% yield: mp 102–108 °C (geometrical isomers); IR (KBr) 1710, 1580, 1570, 1280 (s), 1200, 1070 (s) cm^{-1}; NMR (CDCl$_3$) δ 1.2 (t, 3 H), 4.3 (q, 2 H), 6.55 (d, 1 H), 7.30 (s, 5 H), 7.35 (1 H); mass spectrum, *m/e* 264 (parent peak); UV λ_{max}^{EtOH} 385 nm (3300), 340 (s) (17100), 326 (18300), 228 (17100).

Anal. Calcd for $C_{13}H_{12}O_2S_2$: C, 59.15; H, 4.59; S, 24.21. Found: C, 59.23; H, 4.66; S, 23.97.

2-(*p*-Vinylbenzylidene)-4-phenyl-1,3-dithiole (9). *p*-Vinylbenzaldehyde (2.64 g, 20 mmol) was added under nitrogen at room temperature to a tri-*n*-butylphosphine (4.04 g)–CS$_2$ (excess) complex. Phenylacetylene (2.04 g, 20 mmol) in 50 mL of ether was then added through an addition funnel over 10 min and the solution was stirred 7 h more at room temperature. After filtration and crystallization from carbon tetrachloride, 0.261 g of yellow powder was obtained: mp 228 °C; yield 10%; mass spectrum, *m/e* 294; UV $\lambda_{max}^{CH_2Cl_2}$ 378 nm (27200), 230 (sh) (15000); IR (KBr) 1575 (s), 1525, 1490, 1450, 1400, 1000, 940, 900, 860 (s), 745 (s) cm^{-1}; NMR (CF$_3$CO$_2$H) δ 1.75 (d, 3 H), 5.0 (s, 2 H), 6.2 (q, 1 H), 7.55 (s, 4 H), 7.65 (s, 5 H).

Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.45; H, 4.79. Found: C, 74.30; H, 5.18.

2-Benzylidene-4-phenyl-1,3-dithiole (4). The procedure is the same as above. This compound was obtained in 10% yield: mp 204 °C dec (lit.[4] mp 207 °C); IR (KBr) 1575 (s), 1565 (s), 1480, 1425, 1375 cm^{-1}; NMR (CS$_2$) δ 6.4 (s, 1 H), 6.5 (s, 1 H), 7.2–7.4 (2 peaks, 10 H); mass spectrum, *m/e* 268 (parent peak).

Anal. Calcd for $C_{16}H_{12}S_2$: C, 71.60; H, 4.51. Found: C, 71.46; H, 4.56.

2-Benzylidene-4,5-diphenyl-1,3-dithiole (5). Benzaldehyde (4.24 g, 40 mmol) was added under nitrogen at room temperature to a tri-*n*-butylphosphine (8.10 g, 40 mmol)–CS$_2$ (excess) complex in 50 mL of absolute ether. Tolan (7.12 g, 40 mmol) in 150 mL of absolute ether was then added through an addition funnel over 1 h, and the resulting solution was stirred for 1 week under nitrogen at room temperature. At the end of the reaction, tri-*n*-butylphosphine was swept away by air, and a tolan–dithiole mixture was obtained. After the mixture was crystallized twice from methanol it was sublimed at 50 °C for 2 days to get rid of the tolan. The final pure product was obtained after recrystallization from methanol: yield 5%; mp 124 °C. The low yield is due to the difficult purification steps: IR (KBr) 1591, 1545, 1490, 1440 cm^{-1}; NMR (CDCl$_3$) δ 7.3 (s, 5 H), 7.2 (s, 10 H), 6.45 (s, 1 H); mass spectrum, *m/e* 334 = base peak = parent peak; UV $\lambda_{max}^{CH_3CN}$ 339 nm (21150), 237 (23600).

Anal. Calcd for $C_{22}H_{16}S_2$: C, 76.80; H, 4.68. Found: C, 76.83; H, 4.83.

Catonic Polymerization of Dimethyl 2-(*p*-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate (7). Initiator Preparation. SnCl$_4$ (0.764 g) from a new bottle was injected into a 50-mL flask flushed with nitrogen. Approximately 20 mL of carbon tetrachloride (dried over calcium chloride) was injected into the mixture and the flask was weighed again. The resulting initiator contained 2.42% stannic chloride by weight.

Polymerization. Monomer (5 × 10^{-3} mol, 1.670 g) was dissolved in 5.1 mL of nitrobenzene (5 × 10^{-2} mol) and 4.8 mL of carbon tetrachloride (5 × 10^{-2} mol), and the resulting solution was degassed by bubbling nitrogen through it for 30 min. After the solution was cooled to 0 °C in an ice bath, the initiator (0.334 mL) was injected into the mixture (1% by mole to monomer). The solution was stirred for 48 h. The polymeric solution was precipitated into hot methanol twice and 0.224 g of polymer was obtained with 13% conversion. Some sticky orange oil was also obtained at the bottom of the beaker: NMR (CDCl$_3$) showed broad peaks at δ 1.7, 2.4, 3.7, 5.4, 6.4, 7.0; IR (KBr) 1720 (s), 1580 (s), 1260 (s), 1095 (w), 1030 (w) cm^{-1}; molecular weight 950 (by ebullioscopic method).

Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.50; H, 4.19; S, 19.15. Found: C, 57.35; H, 4.49; S, 19.19.

Anionic Polymerization of Dimethyl 2-(*p*-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate (7). A solution of 1 mmol of monomer in 10 mL of THF was degassed by bubbling nitrogen through it for 30 min and 6.7 × 10^{-2} mL (5% to monomer) of *n*-BuLi (0.75 M in hexane) was injected into the mixture with a hypodermic syringe. After the solution was stirred for 48 h it was poured into methanol and no polymer was found.

Polymerization of Dimethyl 2-(*p*-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate (7) by Concentrated Sulfuric Acid. The monomer (0.500 g) was dissolved in 5 mL of concentrated sulfuric acid and the solution was stirred for 4 h at room temperature. The solution was then poured into ice water, filtered, and washed with water. The polymer was precipitated twice into hot methanol to give 0.42 g of polymer with 85% conversion: NMR ($CDCl_3$) δ 7.1 (4 H), 6.4 (1 H), 3.8 (6 H), 1.0–2.5 (3 H, broad); IR (KBr) 1720 (s), 1580, 1420, 1240 (broad, s), 1095 (w), 1030 (w) cm^{-1}; UV $\lambda_{max}^{CHCl_3}$ 405 nm (1000), 328 (12 500), 238 (12 900); molecular weight 7000 (by ebullioscopic method); η_{inh} = 0.03 in benzene.

Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.50; H, 4.19; S, 19.15. Found: C, 56.79; H, 4.11: S, 19.06.

Copolymerization of Dimethyl 2-(*p*-Vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate (7) by AIBN. Dimethyl 2-(*p*-vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate (1.0 mmol) and comonomer (1.0 mmol) were dissolved in 10 mL of dry benzene and the solution was degassed by bubbling nitrogen through it. After 0.0082 g of AIBN (2.5% by mole to monomers) was added, the resulting solution was refluxed under nitrogen. After precipitation and reprecipitation, low molecular weight alternating copolymer was obtained; η_{inh} = 0.02 in benzene; composition was calculated from sulfur analysis.

Poly[dimethyl 2-(*p*-vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate] (10). *p*-Vinylbenzaldehyde was polymerized according to the procedure of Kinoshita and Schulz[5] for 21 h with 73% conversion. The polymer obtained was insoluble in benzene and slightly soluble in chloroform. The chemical modification was done in THF by reacting the polymer (0.7 g) with carbon disulfide (10 mmol), tri-*n*-butylphosphine (10 mmol), and dimethyl acetylenedicarboxylate (10 mmol) at −23 °C: NMR ($CDCl_3$) δ 1.5 (broad, 3 H), 3.9 (s, 6 H), 6.4 (s, 1 H), 6.6–7.6 (broad, 4 H); IR (KBr) 1720, 1590, 1430, 1260, 1095 (w), 1035 (w) cm^{-1}; UV $\lambda_{max}^{CHCl_3}$ 405 nm (1050), 326 (13 300), 255 (sh) (11 500); η_{inh} = 0.06 in benzene.

Anal. Calcd for $C_{16}H_{14}O_4S_2$: C, 57.50; H, 4.19; S, 19.15. Found: C, 57.46; H, 4.25; S, 15.73.

Cationic Polymerization of Ethyl 2-(*p*-Vinylbenzylidene)-1,3-dithiole-4-carboxylate (8). The initiator contained $SnCl_4$ (2.42% by weight); 2 mmol (0.580 g) of monomer was dissolved in 5 mL of dry nitrobenzene and 4.8 mL of dry CCl_4 and the solution was degassed by bubbling nitrogen through it for 30 min. The orange solution was then cooled to 0 °C and some of the monomer was precipitated out. After 0.67 mL of initiator (5% to monomer) was injected through the rubber cap under nitrogen, all the monomer dissolved immediately to give a dark-orange solution. The solution was then stirred for 48 h at 0 °C under nitrogen. After precipitation into hot methanol, 0.10 g of polymer was obtained with 17% conversion; η_{inh} = 0.03 in benzene.

Anal. Calcd for $C_{15}H_{14}S_2O_2$: C, 62.10; H, 4.86; S, 22.08. Found: C, 62.19; H, 5.06; S, 22.15.

TCNQ-2-Benzylidene-4,5-diphenyl-1,3-dithiole Complex. Hot, saturated acetonitrile solutions of TCNQ (0.204 g, 1 mmol) and dithiole (0.344 g, 1 mmol) were mixed and the resulting solution was concentrated by evaporation at room temperature. After the concentrate was dried, 0.30 g of yellow crystals was isolated: mp 165 °C with dec (sublimation of TCNQ); IR (KBr) 3080 (TCNQ), 2250 (TCNQ), 1595 (dithiole), 1580 (dithiole), and 860 (s) (TCNQ) cm^{-1}; NMR ($CDCl_3$) δ 7.5–7.9 (a, 4 H, TCNQ), 7.4 (s, 5 H), 7.2 (d, 10 H); UV $\lambda_{max}^{CH_2Cl_2}$ 240 nm, 320, 370, 465, 780, 842; mass spectrum, *m*/*e* parent peak = 548, small, base peak = 334 (dithiole), 204 (TCNQ), *p*-CN = 522.

Anal. Calcd for $C_{34}H_{20}N_4S_2$: C, 74.40; H, 3.68; N, 10.21. Found: C, 74.27; H, 3,87; N, 9.98.

Dimethyl 2-Benzylidene-1,3-dithiole-4,5-dicarboxylate–TCNQ Complex. Dithiole (4.72 mmol, 1.455 g) in 35 mL of hot acetonitrile was added dropwise to a 100 mL hot acetonitrile solution of TCNQ (0.965 g, 4.72 mmol). The solution was concentrated and left to sit to crystallize the complex. The yellow crystals were recrystallized from 30 mL of acetonitrile and 0.763 g of yellow crystals was obtained: mp 220 °C (became green); IR (KBr) 1755 (s), 1735 (s), 1590 (s), 1420; NMR ($CDCl_3$) δ 3.80 (d, 12 H), 7.2–7.6 (m, 12 H), 7.8 (s, 4 H); UV $\lambda_{max}^{CH_3CN}$ 840 nm, 820, 795 (sh), 760, 742, 725 (sh), 675, 663, 470 (sh), 420 (sh).

Anal. Calcd for $C_{40}H_{28}N_4S_4O_8$: C, 58.55; S, 15.65; H, 3.44. Found: C, 58.52; S, 15.87; H, 3.54.

TNF–(Dimethyl 2-Benzylidene-1,3-dithiole-4,5-dicarboxylate) Complex (1:1). Dithiole (3.308 g) and 0.315 g (1 mmol) of TNF were dissolved in hot absolute ethanol and a dark green precipitate was obtained immediately. After recrystallization, 0.514 g of dark green finely divided crystals was obtained: mp 145 °C sharp (dithiole mp 100 °C, TNF mp 175–176 °C); yield 85%; IR (KBr) 1730 (s), 1700 (s), 1600, 1580, 1525 (s), 1430, 1340 (s), 1260 (broad), 1080, 1035 cm^{-1}; NMR ($CDCl_3$) δ 9.0 (d, 1 H), 8.7 (d, 1 H), 8.6 (d, 1 H), 8.5 (d, 1 H), 8.4 (d, 1 H), 7.2 (d, 5 H), 6.4 (d, 1 H), 3.9 (s, 6 H); mass spectrum, *m*/*e* base peak = parent peak 315 (TNF), and 308 (dithiole); UV $\lambda_{max}^{CH_2Cl_2}$ 420 nm (sh) (855), 370 (sh) (3400), 322 (12 200), 286 (24 800), 280 (25 100). TNF: UV $i_{max}^{alcohol}$ 336–348 nm (7940), 280 (32600).

Anal. Calcd for $C_{27}H_{17}N_3S_2O_{11}$: C, 52.10; H, 2.75; N, 6.74; S, 10.03. Found: C, 52.26; H, 2.87; N, 6.68; S, 10.13.

Poly[dimethyl 2-(*p*-vinylbenzylidene)-1,3-dithiole-4,5-dicarboxylate]–TNF Complex. Dithiole polymer (84 mg polymerized by sulfuric acid, η_{inh} = 0.03 in benzene) and 81 mg of TNF were dissolved in 1 mL of benzene and the solution was heated to boiling. The dark solution was poured into methanol and dried. Dark green π complex (106 mg) was obtained: IR (KBr) 1730 (s), 1720 (s), 1595 (s), 1440, 1375 (s), 1260 (broad), 1090, 1020 cm^{-1}; NMR ($CDCl_3$) δ 8.4–9.0 (q, broad), 7.1 (broad, 4 H), 6.4 (broad, 1 H), 3.9 (s, 6 H). Integration showed only half of the dithiole heterocycles formed complexes with TNF.

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References and Notes

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