Syntheses and Properties of 2,2′-Binaphtho[1,8-*de*]-1,3-dithiinylidene and Its Selenium Analog, 2-(1,3-Dithiol-2-ylidene)naphtho[1,8-*de*]-1,3-dithiin, and 2-(4*H*-Thiopyran-4-ylidene)naphtho[1,8-*de*]-1,3-dithiin

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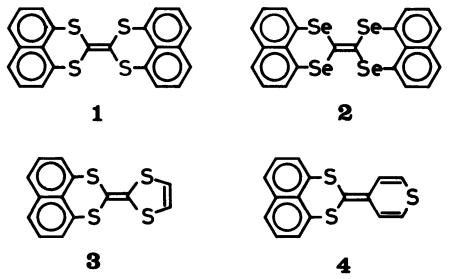
In order to discover new electron donors for conducting charge-transfer complexes, the four title compounds **1**—**4** composed of two heterocycles have been prepared via 1,8-dichalcogen-bridged naphthalene. The cyclic voltammetery indicates that symmetrical **1** and **2** are poor donors, but unsymmetrical **3** and **4** possess considerable donor abilities. The latter compounds are thus capable of forming some crystalline charge-transfer complexes with strong acceptors such as TCNQ, $TCNQF_4$, and DDQ, which are, however, semi-conducting.

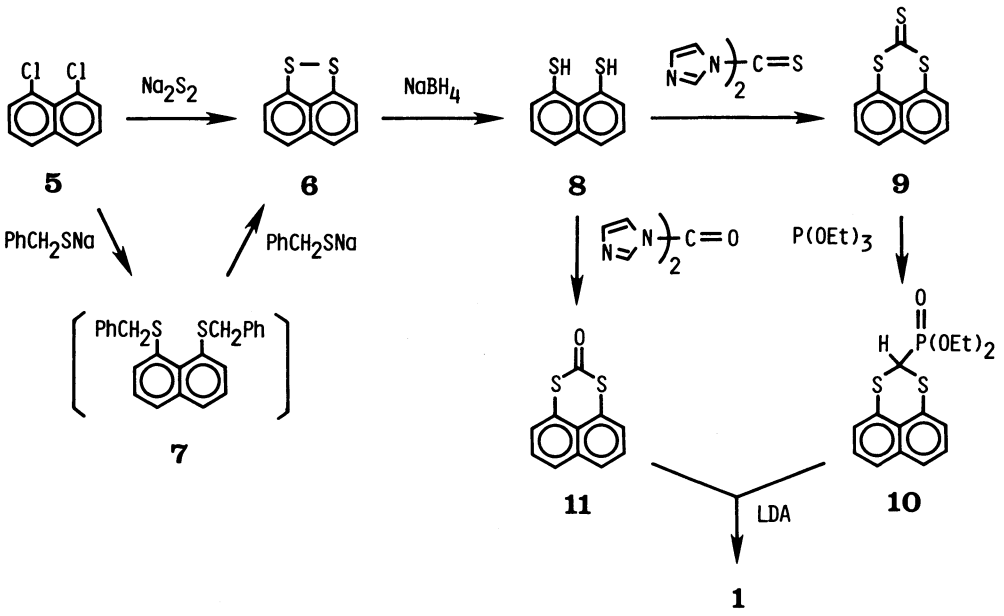
The discovery of tetrathiafulvalene (TTF) and tetraselenafulvalene (TSF), forming highly conducting charge-transfer salts, has stirred considerable interest in searching novel electron donors which have similar behavior.[1] 2,2′-Binaphtho[1,8-*de*]-1,3-dithiinylidene (**1**) and its selenium analog (**2**) involve not only six-membered heterocyclic fragments fused with a naphtho ring, but also the same tetrachalcogenaethylene skeleton as do TTF and TSF. From another viewpoint, they may be regarded as an extended type with ethylene conjugation of 1,8-dichalcogen-bridged naphthalenes, which have been noticeable as a novel class of donor.[2] These unique structural features have prompted us to examine the syntheses and properties of hitherto unknown **1** and **2**. In addition to the symmetrical series, we have studied two unsymmetrical compounds **3** and **4**, into which a structural fragment of TTF or bithiopyranylidene[3] is introduced as the counter heterocycle. They are also



interesting, since unsymmetrical donors often make better conductors than symmetrical ones.[4]

Results and Discussion

Syntheses: The synthetic route of the target molecule **1** is shown in Scheme 1. Nakayama et al. already reported a key intermediate **9**, which was, however, formed as a minor product on photolysis of

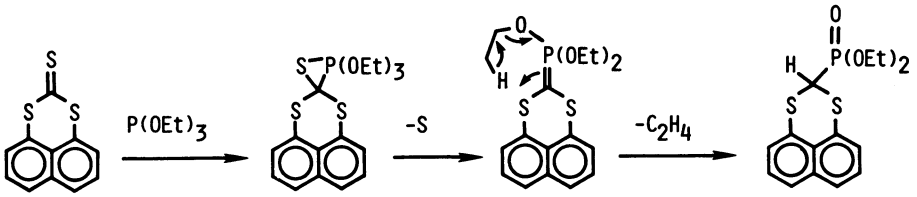


Scheme 1.

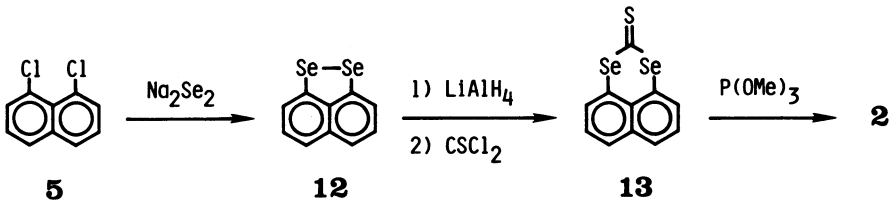
naphtho[1,8-*de*]-1,2,3-thiadiazine in carbon disulfide.[5] We have developed an alternative route to thione **9** via naphtho[1,8-*cd*]-1,2-dithiole (**6**), which is of choice on large-scale preparation. There have been known some methods in which the intermediate **6** may be formed, i.e., a direct thermal reaction of naphthalene and sulfur,[6] multistage reactions starting with diazotization of 8-aminonaphthalene-1-sulfonic acid,[7] and a reaction of 1,8-dilithionaphthalene with sulfur.[2] We have found that a nucleophilic substitution reaction of 1,8-dichloronaphthalene (**5**)[8] with sodium disulfide in hexamethylphosphoric triamide (HMPA) provide a convenient method of obtaining **6** (46% yield). However, it has later turned out that treatment of **5** with excess sodium α-toluenethiolate in HMPA gives a higher yield (78%) of **6** rather than 1,8-bis(benzylthio)naphthalene (**7**) as an expected product. This reaction is supposed to involve the initial substitution reactions to provide **7**, followed by reductive fission of the benzyl-S bond with excess sodium α-toluenethiolate and finally air-oxidation of the resulting 1,8-naththalenedithiolate forming S–S bond. Reduction of **6** with sodium borohydride in tetrahydrofuran-ethanol at RT gave almost quantitatively 1,8-naphthalenedithiol (**8**), which was subsequently treated with *N,N'*-thiocarbonyldiimidazole to afford **9** in 94% yield. Symmetrical TTF derivatives are generally prepared by desulfurizing coupling of two identical 1,3-dithiole-2-thiones using a phosphorus reagent.[9] However, all such conventional attempts to convert **9** into the target molecule **1** were unsuccessful. Treatment of **9** with triethyl phosphite at 110 °C gave diethyl [naphtho[1,8-*de*]-1,3-dithiin-2-yl]phosphonate (**10**) in 92% yield, though the other phosphorus reagents such as trimethyl phosphite and triphenylphosphine led to unidentified products. A plausible mechanism for the formation of **10** is shown in Scheme 2. However, **10** is available for another approach to **1** using a Wittig modification developed by Wadsworth and Emmons.[10] In this connection, naphtho[1,8-*de*]-1,3-dithiin-2-one (**11**) as a counterpart was prepared in 97% yield from a reaction of dithiol **8** and *N,N'*-carbonyldiimidazole. Thus, **10** was treated with lithium diisopropylamide at −78 °C to generate the corresponding phosphonate carbanion, which was then allowed to react with **11**, giving the desired product **1** in 92% yield.

The synthesis of the selenium analog **2** was carried out in a similar, but shorter route as shown in Scheme 3. Thus, a reaction of **5** with sodium diselenide in HMPA at 100 °C gave naphtho[1,8-*cd*]-1,2-diselenole (**12**) in 69% yield. The reduction of **12** with lithium aluminium hydride at RT in THF, followed by treatment with thiophosgene produced naphtho[1,8-*de*]-1,3-diselenin-2-thione (**13**) in 45% yield. In contrast to the above sulfur case, a reaction of **13** with trimethyl phosphite in toluene under reflux directly gave the desired product **2** in 66% yield.

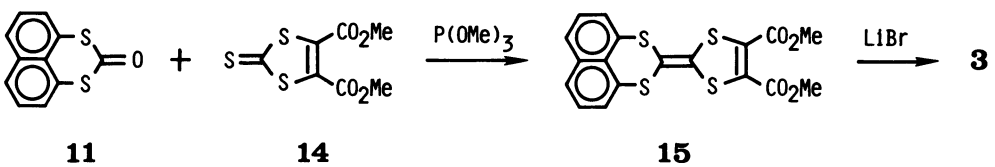
The synthetic route of unsymmetrical compound **3**



Scheme 2.



Scheme 3.

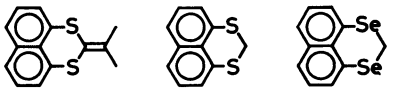


Scheme 4.

is shown in Scheme 4. A cross coupling reaction between **11** and dimethyl 2-thioxo-1,3-dithiole-4,5-dicarboxylate (**14**)[11] in benzene containing trimethyl phosphite at reflux smoothly proceeded to afford diester **15** in 45% yield. Hydrolysis/decarboxylation of **15** occurred on treatment with lithium bromide in HMPA at 150 °C, giving the desired compound **3** in 70% yield.

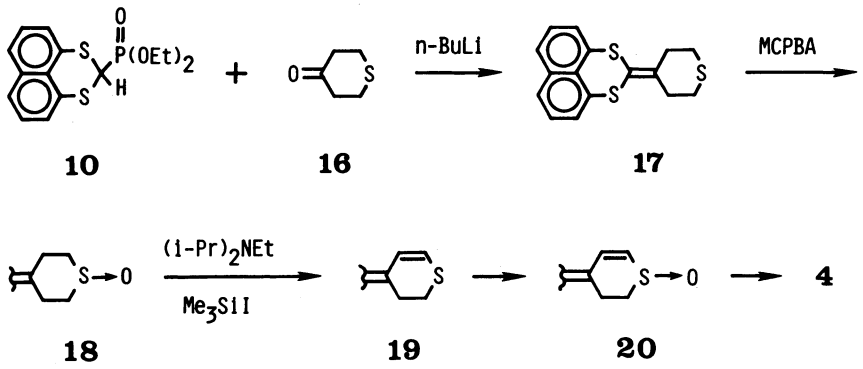
The synthetic route of another unsymmetrical compound **4** is shown in Scheme 5. The phosphonate carbanion from **10** was treated with 4*H*-thiopyran-4-one (**16**) to give tetrahydro derivative **17** in a quantitative yield. Direct conversion of **17** to **4** using chloranil or DDQ as a dehydrogenating agent failed. We then adopted a stepwise route via the conversion of sulfoxide to vinyl sulfide according to the procedure of Miller and Mckean.[12] Thus, sulfide **17** was oxidized with *m*-chloroperbenzoic acid in dichloromethane at RT to sulfoxide **18** in 63% yield, which was subsequently treated with *N*,*N*′-diisopropylethylamine and iodotrimethylsilane in dichloromethane at 0 °C to give dihydro derivative **19** in 86% yield. The same reactions were repeated for **19**, giving the desired product **4** in 43% overall yield.

In addition, three reference compounds **21**—**23** were prepared for spectroscopic comparison. Thus, **21** was accessible in 95% yield from a reaction between the phosphonate anion of **10** and acetone. Compounds **22** and **23** were obtained from treatment of diiodomethane with 1,8-naphthalenedithiolate in 26% yield and with the diselenolate in 32% yield, respectively.



21 **22** **23**

Properties: Table 1 summarizes the UV data as well as oxidation potentials of **1**—**4** together with reference compounds **21**—**23**. All the compounds **1**—**4** have two strong absorptions around 240 and 350 nm in the electronic spectra. The longer wavelength absorptions extend to visible regions, resulting in yellow or orange coloration. These absorptions very closely resemble the corresponding ones of reference compounds **21**—**23** in wavelength except in intensity. This evidently indicates that the principal chromophor is 1,8-dichalcogenonaphthalene and an extended



10 **16** **17** **18** **19** **20** **4**

Scheme 5.

Table 1. UV Data and Oxidation Potentials of **1**—**4** and Reference Compounds **22**—**24**

Compound	Absorption maximum/nm (Intensity/ε)[a]	Oxidation peak/V[b]
1	239(56600), 352(30700)	1.19(1.14)[c]
2	244(47500), 352(25800)	1.17
3	243(33100), 326(21400), 339sh(13800)	0.87(0.79)[c], 1.22
4	244(31500), 354(38800)	0.66(0.76)[c], 1.08
21	246(36300), 268sh(6100), 337sh(10500), 350(11600)	1.28
22	246(26400), 274(2190), 339sh(9890), 348(10800)	1.36
23	255(14200), 354(9250)	1.21

a) Measured in tetrahydrofuran. b) Measured at 100 mV s^{-1} scan rate in benzonitrile solution (10^{-3}—10^{-4} mol dm^{-3} with added tetrabutylammonium perchlorate (0.1 mol dm^{-3}) using a Ag/AgCl reference electrode and platinum working and counter electrodes. c) Values in parentheses indicate half-wave oxidation potentials.

Table 2. Charge-Transfer Complexes of **3** and **4**

Complex	Appearance	DP[a]/°C	Found (Calcd)[c]/%			Conductivity[d]/S cm^{-1}
			C	H	N	
3·DDQ	Dark brown powder from chloroform	220	49.10 (49.72	1.45 1.52	5.20 5.27)	2.3×10^{-7}
3·$TCNQF_4$	Dark green powder from chloroform	187—188[b]	53.78 (53.79	1.33 1.39	9.48 9.65)	4.4×10^{-3}
4·DDQ	Black powder from acetonitrile	130	54.35 (54.86	1.88 1.92	5.95 5.33)	6.5×10^{-5}
4·TCNQ	Black needles from acetonitrile	179—184[b]	66.87 (66.91	2.94 2.81	10.39 11.15)	6.8×10^{-8}
4·$TCNQF_4$	Deep green powder from acetonitrile	225	58.76 (58.53	1.68 1.75	9.67 9.75)	1.8×10^{-7}

a) Decomposition temperature. b) With melt. c) Calculated as 1:1 stoichiometry of donor and acceptor. d) Measured on compressed pellets with a two-probe method at room temperature.

conjugation through the central olefin between the two chromophors is not significant. A structural consideration of **1** and **2** on a molecular model favors nonplanar conformers which are somewhat bent at the sulfur or selenium atoms. This nonplanarity is certainly responsible for reduction in extended conjugation.

The cyclic voltammetry of **21**—**23** demonstrates irreversible oxidation at 1.21—1.36 V vs. Ag/AgCl reference electrode in benzonitrile. On the other hand, **1** undergoes oxidation at a somewhat lower potential (1.19 V) and keeps a reversible redox cycle with a half-wave potential at 1.14 V, which is, however, still too high as an electron donor. The somewhat easier oxidation of **1** and the higher stability of the resulting radical cation, contrary to the above spectroscopic discussion, suggest the existence of some conjugation through the central olefin. The selenium analog **2** unlike **1** shows an irreversible oxidation, whose peak potential (1.17 V) is the almost same as that of **1** or a reference compound **23**. Thus, the substitution of selenium for sulfur in **1** does not serve to enhance its donor character, but rather leads to ready decomposition of the radical cation owing to introduction of labile C–Se bond relative to C–S bond. On the other hand, unsymmetrical compounds **3** and **4** have two oxidation steps, the first of which is reversible and the second is irreversible. The first oxidation potentials (0.87 V for **3** and 0.66 V for **4**) are drastically lower than those of **1** and **2**. Since the counter heterocyclic fragments can take aromatization in the oxidation state, i.e., 1,3-dithiolylium and thiopyranylium cations, they certainly make a significant contribution to the ready oxidations.

Owing to their poor donor strength, **1** and **2** could not form any charge-transfer complexes even with strong electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$), and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). On the other hand, **3** and **4** bearing improved donor abilities formed deeply colored 1:1 charge-transfer complexes with such acceptors. As summarized in Table 2, the electrical conductivities measured on compressed pellets with a two probe method are 10^{-3}—10^{-8} S·cm^{-1}. This semi-conducting behavior suggests a mixed stacking mode of alternate donor and acceptor in the crystal structures.[13]

Experimental

General. Melting points are uncorrected. All solvents are of reagent grades. NMR measurements were made on a JEOL PMX-60 (60 MHz) or a Bruker-WM 360 spectrometer (360 MHz) using TMS as an internal standard. IR spectra were taken on a Hitachi 260-30 spectrophotometer, and MS spectra on a JEOL JMS-DX 300 spectrometer at 70 eV using a direct insertion technique. Electronic spectra were recorded on a JASCO UVIDEC-610A spectrophotometer. Cyclic voltammetry was performed on a Hokuto Denko HA-301 potentiostat and a Hokuto Denko HB-104 function generator.

Naphtho[1,8-*cd*]-1,2-dithiol (6). A) With Sodium α-Toluenethiolate. Into a stirred solution of sodium α-toluenethiolate, which was in situ prepared from α-toluenethiol (42.3 cm^3, 0.36 mol) and sodium hydride (60% oily, 15.8 g, 0.40 mol) in HMPA (400 cm^3), was added a solution of 1,8-dichloronaphthalene (**5**)[7] (11.8 g, 60 mmol) in HMPA (50 cm^3) under argon. The mixture was heated at 160—165 °C for 17 h and cooled to RT. After water (500 cm^3) was added, it was vigorously stirred with bubbling air for 20 h, poured into water, and extracted with benzene. The extract was thoroughly washed with water, dried ($MgSO_4$), and concentrated in vacuo. The resulting solid was purified by column chromatography on silica gel with hexane and then recrystallization from hexane to give **6** as

reddish brown plates (8.95 g, 78%): 123 °C (lit,[6] 116 °C); ^{1}H NMR (60 MHz, CCl_4) δ=7.1—7.7 (ABC m).

B) With Sodium Disulfide. A mixture of sulfur (48 mg, 1.5 mmol) and sodium (38 mg, 1.65 mmol) was heated at 110 °C in dry HMPA (3 cm^3) for 2.5 h under argon. Into the resulting blue solution of sodium disulfide was added a solution of **5** (99 mg, 0.5 mmol) in dry HMPA (2 cm^3). The mixture was heated at 150 °C for 27 h, poured into water, and extracted with benzene. In the same way as described in Method A, compound **6** was obtained from the extract (44 mg, 46%).

1,8-Naphthalenedithiol (8). A solution of **6** (9.51 g, 500 mmol) in dry THF (100 cm^3) was added into an ice-cooled suspension of sodium borohydride (5.00 g, 132 mmol) in ethanol (90 cm^3) under argon. The mixture was stirred for 30 min, quenched with 10% HCl, and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated in vacuo to give **8** (9.45 g, 98%). Recrystallization from THF-hexane in an argon atmosphere afforded colorless leaflets: mp 122 °C (lit,[5b] 115 °C); IR(KBr) 2450, 2520 cm^{-1} (S-H); ^{1}H NMR (60 MHz, CCl_4) δ=3.97 (s, 2H), 6.95—7.65 (ABC m, 6H).

Naphtho[1,8-*de*]-1,3-dithiin-2-thione (9). A solution of *N,N′*-thiocarbonyldiimidazole (1.39 g, 7.04 mmol) in dry THF (30 cm^3) was slowly added into a stirred solution of **8** (1.22 g, 6.40 mmol) in dry THF (30 cm^3) at −15—−20 °C under argon. The mixture was gradually warmed to RT and allowed to stand overnight. After concentration in vacuo, the resulting solid was dissolved in chloroform, washed with water, and dried ($MgSO_4$). The solvent was evaporated, and column chromatography of the residue on silica gel with benzene gave **9** (1.40 g, 94%): orange needles from benzene-hexane, mp 201—202 °C (lit,[4] 199—201 °C); IR(KBr) 1040 cm^{-1} (C=S); ^{1}H NMR (60 MHz, $CDCl_3$) δ=7.1—7.7 (ABC m).

Diethyl [Naphtho[1,8-*de*]-1,3-dithiin-2-yl]phosphonate (10). Thione **9** (113 mg, 0.482 mmol) was heated at 110 °C in triethyl phosphite (6 cm^3) for 2 h under argon. After concentration in vacuo, the residue was filtered through a short column of silica gel with chloroform and then recrystallized from benzene-hexane to give **10** as colorless columns (150 mg, 92%): mp 120 °C; IR (KBr) 1243 (P=O), 1030, 1010, 970, 950 cm^{-1} (P-O-C); ^{1}H NMR (60 MHz, CCl_4) δ=1.20 (t, J_{CH-CH}=7.4 Hz, 6H), 4.02 (d, J_{CH-P}=17 Hz, 1H), 7.2—7.7 (m, 6H); Anal. ($C_{15}H_{17}O_3S_2P$) C, H.

Naphtho[1,8-*de*]-1,3-dithiin-2-one (11). A solution of *N,N′*-carbonyldiimidazole (357 mg, 2.2 mmol) in dry THF (15 cm^3) was slowly added into a stirred solution of **8** (385 mg, 2.0 mmol) in dry THF (30 cm^3) at −15 °C under argon. The mixture was warmed to RT and allowed to stand for several hours. After concentration in vacuo, the resulting solid was filtered through a short column of silica gel with hexane-benzene (1:1) and recrystallized from benzene-hexane to give **11** as colorless needles (391 mg, 97%): mp 140 °C; IR (KBr) 1630 cm^1 (C=O); ^{1}H NMR (60 MHz, CCl_4) δ=7.1—7.7 (ABC m); Anal. ($C_{11}H_6OS_2$) C, H.

2,2′-Binaphtho[1,8-*de*]-1,3-dithiinylidene (1). A solution of LDA (1 mol m^{-3}, 1.05 cm^3) in THF-hexane (1:2.7) was dropwise added into a stirred solution of **10** (340 mg, 1.0 mmol) in dry THF (10 cm^3) at −78 °C during 10 min under argon. A solution of **11** (240 mg, 1.1 mmol) in dry THF (6 cm^3) was successively added, and then the mixture was gradually warmed to 0 °C. The resulting precipitate was collected by filtration, washed with water, and dried. Recrystallization from carbon disulfide gave pale yellow fine prisms of **1** (372 mg, 92%): mp 297 °C; ^{1}H NMR (360 MHz, CS_2) δ=7.22—7.28 (m, 8H), 7.486 (dd, J=7.37 and 1.92 Hz, 4H); MS *m/z* 404 (M$^+$); Anal. ($C_{22}H_{12}S_4$) C, H.

Naphtho[1,8-*cd*]-1,2-diselenole (12). A mixture of selenium powder (4.03 g, 51 mmol) and sodium (1.17 g, 51 mmol) was heated at 120 °C in dry HMPA (35 cm^3) for 4 h under argon. Into the resulting reddish brown solution of sodium diselenide was added a solution of **5** (2.95 g, 15 mmol) in dry HMPA (15 cm^3). The mixture was heated at the same temperature for additional 19 h, poured into water (450 cm^3), and extracted with benzene. The extract was thoroughly washed with water, dried ($MgSO_4$), and concentrated in vacuo. The residual solid was purified by column chromatography on silica gel with benzene and then gel-permeation liquid chromatography with chloroform to give **12** (2.95 g, 69%): deep violet needles from hexane, mp 124 °C (lit,[2] 127—129 °C); ^{1}H NMR (60 MHz, CCl_4) δ=7.1—7.7 (ABC m).

Naphtho[1,8-*de*]-1,3-diselenin-2-thione (13). Compound **12** (142 mg, 0.50 mmol) was treated with LAH (10.4 mg, 0.275 mmol) in dry THF (7 cm^3) for 40 min at RT. Into the mixture at −30—−40 °C was slowly added a solution of thiophosgene (46 mm^3, 0.60 mmol) in dry THF (7 cm^3). The mixture was gradually warmed to RT and stirred further 1.5 h. After concentration, the residue was poured into aq. satd. ammonium chloride and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and evaporated. The resulting solid was purified by column chromatography on silica gel with hexane and then gel-permeation liquid chromatography to give **13** (74 mg, 45%): orange needles from hexane, mp 153—154 °C; IR (KBr) 1021 cm^{-1} (C=S); ^{1}H NMR (60 MHz, $CDCl_3$) δ=7.2—7.9 (ABC m); Anal. ($C_{11}H_6SSe_2$) C, H.

2,2′-Binaphtho[1,8-*de*]-1,3-diseleninylidene (2). A mixture of **13** (73 mg, 0.22 mmol), trimethyl phosphite (0.10 cm^3, 0.88 mmol), and toluene (3 cm^3) was heated at reflux for 4 h. The resulting precipitate was collected by filtration, washed with cold acetone, and recrystallized from toluene to give pale yellow fine crystals of **2** (43 mg, 66%): mp 287—287.5 °C; ^{1}H NMR (360 MHz, CS_2) δ=7.286 (t, J=7.7 Hz, 4H), 7.476 (bd, J=7.3 Hz, 4H), 7.610 (bd, J=8.1 Hz, 4H); MS *m/z* 594 (M$^+$); Anal. ($C_{22}H_{12}Se_4$) C, H.

2-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]naphtho[1,8-*de*]-1,3-dithiin (15). A mixture of **11** (1.53 g, 7 mmol) and dimethyl 2-thioxo-1,3-dithiol-4,5-dicarboxylate (**14**)[10] (3.50 g, 14 mmol) was refluxed in dry benzene (50 cm^3) containing trimethyl phosphite (21 cm^3) for 1.5 h under argon. After concentration in vacuo, the residue was chromatographed on silica gel with benzene to give **15** (1.31 g, 45%): orange fine needles from hexane-benzene, mp 217—218 °C; IR (KBr) 1730, 1710 cm^{-1} (C=O); ^{1}H NMR (60 MHz, $CDCl_3$) δ=3.80 (s, 6H), 7.2—7.8 (m, 6H); Anal. ($C_{18}H_{12}O_4S_4$) C, H.

2-(1,3-Dithiol-2-ylidene)naphtho[1,8-*de*]-1,3-dithiin (3). A solution of diester **15** (1.31 g, 3.12 mmol) and lithium bromide monohydrate (3.27 g, 31.2 mmol) in HMPA (50 cm^3) was heated at 100 °C for one h and then at 150 °C for another h. The mixture was cooled to RT, poured into

water, and extracted with benzene. The extract was washed with water, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel with hexane–benzene (1:1) to give **3** (0.66 g, 70%): lemon yellow prisms from benzene–hexane, mp 173.5—175 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ=6.33 (s, 2H), 7.2—7.8 (m, 6H); MS *m/z* 304 (M^+); Anal. ($C_{14}H_8S_4$) C, H.

2-(Tetrahydro-4*H*-thiopyran-4-ylidene)naphtho[1,8-*de*]-1,3-dithiin (17). A hexane solution of butyllithium (1.6 mol dm^{-3}, 9.4 cm^3, 15 mmol) was dropwise added into a stirred solution of **10** (5.11 g, 15 mmol) in dry THF (200 cm^3) at −78 °C under argon. A solution of 4*H*-thiopyran-4-one (**16**) (1.92 g, 16.5 mmol) in dry THF (30 cm^3) was subsequently added. The mixture was warmed to RT over a period of 3 h. After the solvent was evaporated, the residue was dissolved in chloroform, washed with brine, and dried ($MgSO_4$). After concentration, the residue was chromatographed on silica gel with benzene to give **17** (4.49 g, 99%): colorless plates from hexane, mp 142—143 °C; ^{1}H NMR (60 MHz, CCl_4) δ=2.85 (A_2B_2 m, 8H), 7.1—7.6 (ABC m, 6H); Anal. ($C_{16}H_{14}S_3$) C, H.

4-[Naphtho[1,8-*de*]-1,3-dithiin-2-ylidene]tetrahydro-4*H*-thiopyran *S*-Oxide (18). A solution of MCPBA (4.0 g, 23.2 mmol) in dichloromethane (20 cm^3) was dropwise added into a solution of **17** (4.54 g, 15 mmol) in dichloromethane (100 cm^3) at −15—−20 °C. The mixture was stirred at 0 °C for 2 h and then at RT for 30 min. It was successively washed with aq. satd. $NaHSO_3$, aq. 5% $NaHCO_3$, and water. The solution was dried ($MgSO_4$) and concentrated in vacuo. The residue was chromatographed on silica gel with chloroform to give **18** (3.0 g, 63%): colorless leaflets from benzene–hexane, mp 203—206 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ=2.95 (A_2B_2 m, 8H), 7.2—7.8 (ABC m, 6H); Anal. ($C_{16}H_{14}OS_3$) C, H.

2-(2,3-Dihydro-4*H*-thiopyran-4-ylidene)naphtho[1,8-*de*]-1,3-dithiin (19). Iodotrimethylsilane (3.58 cm^3, 25.2 mmol) was dropwise added into a stirred solution of **18** (4.0 g, 12.6 mmol) and *N*,*N*-diisopropylethylamine (4.81 cm^3, 27.6 mmol) in dry dichloromethane (100 cm^3) at 0 °C under argon. The mixture was stirred at 0 °C for 4 h and then at RT for 2 h, diluted with ether (100 cm^3), and poured into 10% sulfuric acid. The organic layer was separated, succesively washed with aq. 5% $NaHCO_3$ and with water, and dried ($MgSO_4$). After concentration in vacuo, the residual solid was chromatographed on silica gel with chloroform to give **19** (3.25 g, 86%): pale yellow leaflets from benzene–hexane, mp 117—118 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ=2.97 (A_2B_2 m, 4H), 6.35 (d, J=10 Hz, 1H), 6.99 (d, J=10 Hz, 1H), 7.1—7.8 (ABC m, 6H); Anal. ($C_{16}H_{12}S_3$) C, H.

4-[Naphtho[1,8-*de*]-1,3-dithiin-2-ylidene]-2,3-dihydro-4*H*-thiopyran *S*-Oxide (20). Compound **20** was obtained in 63% yield by oxidation of **19** with MCPBA in a similar manner as described for the synthesis of **18**: pale yellow crystals from acetone–dichloromethane, mp 158—160 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ=3.0 (A_2B_2 m, 4H), 6.42 (d, J=10 Hz, 1H), 7.0—7.8 (m, 7H); Anal. ($C_{16}H_{12}OS_3$) C, H.

2-(4*H*-Thiopyran-4-ylidene)naphtho[1,8-*de*]-1,3-dithiin (4). Compound **4** was obtained in 68% yield from **20** by the same method as described for the conversion of **18** into **19**: orange needles from benzene–hexane, mp 155—157 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ=6.37 (d, J=10 Hz, 2H), 7.0—7.8 (m, 8H); Anal. ($C_{16}H_{10}S_3$) C, H.

2-Isopropylidenenaphtho[1,8-*de*]-1,3-dithiin (21). Into a solution of **10** (42 mg, 0.12 mmol) in dry THF (2 cm^3) at −78 °C under argon were dropwise added a solution of LDA (1 mol m^{-3}, 0.13 cm^3) in THF–hexane (1:2.7) and subsequently a solution of acetone (9:6 mm^3, 0.13 mmol) in dry THF (0.5 cm^3). The mixture was gradually warmed to RT, poured into aq. satd. ammonium chloride, and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel with hexane to give **21** (28 mg, 95%): colorless prisms from hexane, mp 106 °C; ^{1}H NMR (60 MHz, CCl_4) δ=2.06 (s, 6H), 7.1—7.6 (ABC m, 6H); Anal. ($C_{14}H_{12}S_2$) C, H.

Naphtho[1,8-*de*]-1,3-dithiin (22). A solution of **8** (1.05 g, 5.26 mmol) and diiodomethane (1.41 g, 5.26 mmol) in dry THF (300 cm^3) was dropwise added into a stirred suspension of sodium hydride (60% oily, 505 mg, 12.6 mmol) in dry THF (100 cm^3) at RT under argon. The addition took 40 h. After the addition, stirring was continued further 6 h. The reaction mixture was concentrated in vacuo, poured into water, and extracted with chloroform. The extract was washed with water, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel with hexane–benzene to give colorless plates of **22** (280 mg, 26%): mp 124—125 °C; ^{1}H NMR (60 MHz, CCl_4) δ=4.01 (s, 2H), 6.95—7.70 (ABC m, 6H); Anal. ($C_{11}H_8S_2$) C, H.

Naphtho[1,8-*de*]-1,3-diselenin (23). A solution of **12** (568 mg, 2.0 mmol) in dry THF (25 cm^3) was slowly added into a stirred suspension of sodium borohydride (267 mg, 7.06 mmol) in ethanol (8 cm^3) at RT under argon. It was then transferred into a dropping funnel. A solution of diiodomethane (836 mg, 3.2 mmol) in dry THF (25 cm^3) was placed in another dropping funnel. Both solutions were simultaneously added into a stirred THF solution (10 cm^3) at RT over a period of 3 h. The mixture was concentrated, dissolved in chloroform, and washed with water. After it was dried ($MgSO_4$) and again concentrated, the residue was purified by column chromatography on silica gel with hexane–chloroform (1:1) and then gel-permeation liquid chromatography with chloroform to give **23** (190 mg, 32%): pale orange leaflets from hexane, mp 128.5 °C; ^{1}H NMR (60 MHz, CCl_4) δ=3.91 (s and t, J_{Se-C-H}=7 Hz, 2H), 7.0—7.7 (ABC m, 6H); Anal. ($C_{11}H_8Se_2$) C, H.

Preparation of Charge-Transfer Complexes. All CT complexes described in this paper were prepared by mixing the two hot saturated solutions of donor and acceptor in chloroform or acetonitrile. The deeply colored complexes precipitated out immediately or on cooling in a refrigerator, which were collected by filtration.

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