$C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.95; H, 5.57.

3,7-*exo*-*syn*-Hexacyclo[12.2.1.1^{2,8}.1^{9,12}.0^{3,7}.0^{11,15}]nonadeca-1(17),5,9(18)-triene-4,10,16-trione (29). The diketo enone **28** (50 mg, 0.17 mmol) was sublimed at 200 °C (0.2 Torr) through a quartz tube preheated to 650 °C (±10 °C).[8] Chromatography over silica gel (10 g) in ethyl acetate gave starting **28** (14 mg, 28%) followed by trisenone **29** (18 mg, 36%), mp 277–278 °C, on crystallization from CH_2Cl_2–hexane: IR ν_{max} (KBr): 3050, 2950, 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.7–7.5 (dd, J_1 = 6 Hz, J_2 = 3 Hz, 1 H, *H*C=CHC=O), 6.9–6.7 (m, 2 H, *H*C=CC=O), 6.30–6.08 (dd, J_1 = 6 Hz, J_2 = 2 Hz, 1 H, HC=C*H*C=O), 4.7–4.4 (m, 1 H), 4.08 (d, J = 6 Hz, 1 H), 3.7–1.5 (series of m, 10 H); ^{13}C NMR ($CDCl_3$) δ 212.7, 207.7 (2 C), 167.0, 59.3, 159.2, 151.6, 150.9, 134.7, 57.9, 57.0, 49.5, 47.0, 46.8, 45.6, 44.3, 40.4, 39.0, 28.9. Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.29; H, 5.67.

3,7-*exo*-*syn*-Hexacyclo[12.2.1.1^{2,8}.1^{9,12}.0^{3,7}.0^{11,15}]nonadeca-1(17),5,9(18)-triene-4,10,16-trione (29) Directly from 13. The bisenone **13** (50 mg, 0.20 mmol) was reacted with $Co_2(CO)_8$ (70 mg, 0.20 mmol) as described above to furnish **33** (35 mg, 33%). This material was identical with the sample characterized in the previous experiment.

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Registry No. 1, 4493-23-6; **3**, 126984-41-6; **10**, 119364-65-7; **10** diol, 127277-46-7; **11**, 119364-64-6; **12**, 126984-42-7; **13**, 127062-56-0; **14**, 127062-57-1; **15**, 126984-43-8; **16**, 126984-44-9; **17**, 126984-45-0; **19**, 126984-46-1; **19** diol, 126984-49-4; **21**, 136911-85-8; **23**, 126984-47-2; **24**, 136983-99-8; **25**, 136911-86-9; **26**, 136911-87-0; **27**, 136911-88-1; **28**, 136984-00-4; **29**, 136984-01-5; **30**, 82253-87-0; **31**, 82217-29-6; **32**, 106092-82-4; **33**, 130563-14-3; **34**, 136911-89-2; **35**, 136911-90-5; Cl_3CCOCl, 76-02-8; C_2H_2, 74-86-2.

Synthesis and Properties of Substituted 1,6-Dioxapyrene Donors

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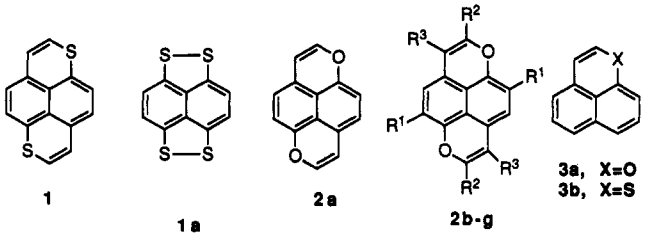
The synthesis of substituted 1,6-dioxapyrenes, **2b–g**, from 2,6-dipropyl-1,5-naphthalenediol (**7a**) or 2,6-dimethyl-1,5-naphthalenediol (**7b**) is described. Diol **7a** was prepared by Claisen allylic rearrangement followed by reduction, and **7b** was prepared by Mannich reaction of 1,5-naphthalenediol followed by base-promoted hydrogenolysis. The 1,6-dioxapyrenes can be oxidized to stable cation radicals at +0.2–0.35 V vs SCE and to dications at +0.8–1.20 V. The preparation of some tetracyanoquinodimethane salts and binary cation radical salts of the 1,6-dioxapyrenes is reported.

Introduction

Heterocyclic analogues of pyrenes are good electron donors. 1,6-Dithiapyrene[1] (**1**) has been demonstrated to give a highly conducting 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) salt.[2] Other 1,6-dithiapyrenes substituted with alkyl, aryl, alkoxy, or alkylthio substituents have similarly been found to form conducting molecular solids.[3,4] The 1,6-heteropyrenes are electronic equivalents of the donors dehydrotetrathianaphthazarin[5] (**1b**) and its selenium analogue.[6] We have been interested in studying the



1 **1a** **2a** **2b-g**

effect of oxygen in heterocyclic donor systems such as the 1,6-dioxapyrenes **2a–g** because oxygen is smaller and less polarizable than the sulfur and selenium heteroatoms. When 1,6-dioxapyrenes are used to generate conducting salts consisting of uniform stacks of molecules, we expect to obtain an increase in bandwidths as well as electronically more one-dimensional materials in comparison with the sulfur and selenium containing materials. The purpose of this work was to identify 1,6-dioxapyrenes capable of forming stoichiometric salts. In a second phase we intend to prepare the sulfur and selenium analogues of selected 1,6-dioxapyrenes and evaluate in detail the effects of the heteroatoms in an isostructural series of 1,6-dichalcogenpyrene based conducting materials. We report the preparation[7] six new alkyl and aryl derivatives, **2b–g**, of 1,6-dioxapyrene, and we have attempted to prepare the parent system. Very recently **2a** was prepared[8] by a procedure different from the general procedure presented here. The analogous oxaphenalene[9a] (**3a**) and thiaphenalene[9b] (**3b**) have been described previously. Several conducting solids based on other oxygen-containing donors have been pre-

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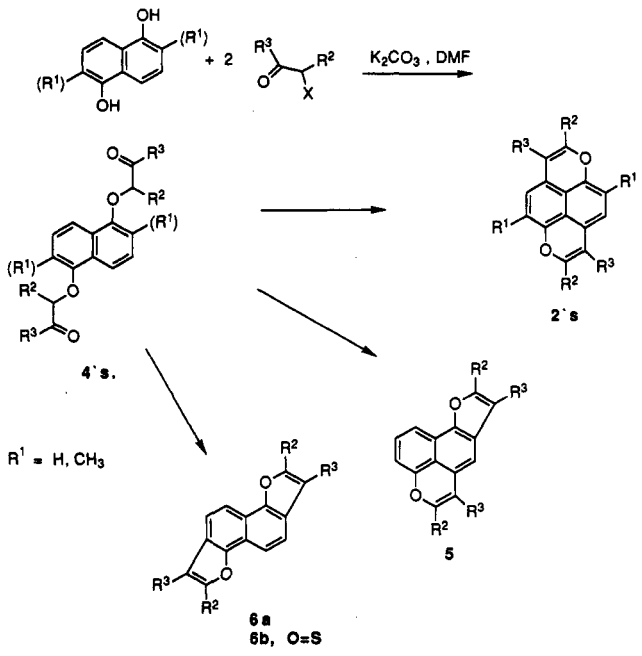
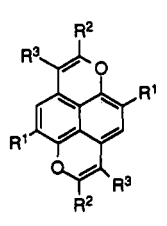
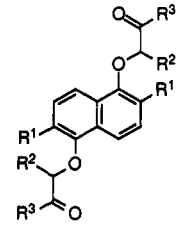
Scheme I



pared and investigated[10-12] partly for the same reasons as given here. It should also be mentioned that an early attempt to obtain **2a** did not give measurable amounts.[13]



2b-g



4b-g

Compounds		R^1	R^2	R^3
2a		H	H	H
2b	**4b**	CH_3	H	CH_3
2c	**4c**	CH_3	CH_3	CH_3
2d	**4d**	CH_3	H	C_2H_5
2e	**4e**	C_3H_7	H	CH_3
2f	**4f**	CH_3	H	C_6H_5
2g	**4g**	CH_3	CH_3	C_6H_5

The substituted 1,6-dioxapyrenes **2b–g** are excellent electron donors[7b] and exhibit, in solution, lower electrochemical oxidation potentials than the corresponding 1,6-dithiapyrenes. Some members of the series **2b–g** form stoichiometric semiconducting molecular solids as described below.

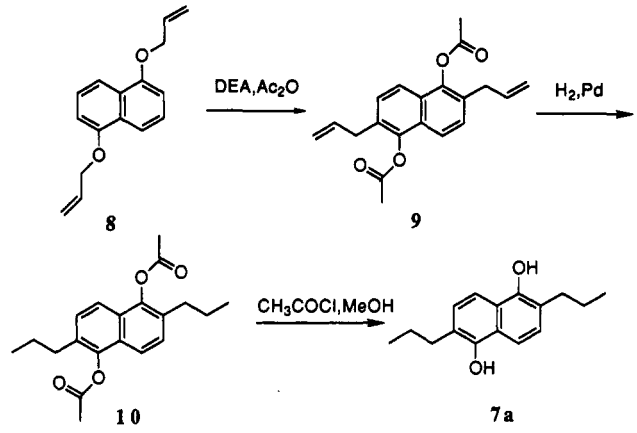
Results and Discussion

The 1,6-dioxapyrenes **2b–g** were obtained by acid-catalyzed ring closure of the bis(2-oxoalkyl) ethers of 2,6-dialkyl-1,5-naphthalenediols (**4b–g**) as outlined in Scheme I. In this type of reaction the products **2**, **5**, and **6** are possible, depending on the regioselectivity of the ring-closure reaction. We found that when compound **4** is unsubstituted in the 2- and 6-positions, the furo[2,3-*f*]-naphtho[1,2-*b*]furanes **6a** invariably were the products,[13] even under very mild reaction conditions.[14] This was contrary to the findings in the analogous sulfur series, where 1,6-dithiapyrenes (**1**) were the kinetically favored products, whereas **6b**'s were the thermodynamically favored products.[1,4] In no case were products corresponding to structure **5** identified. Likewise, in the preparation of thiaphenalene (**3b**) it was a problem to achieve regioselectivity. In that case the 2-position was blocked with a halogen, which was removed by metalation and hydrolysis after ring closure.[9b] Our attempts to prepare **2a** similarly by starting from 2,6-dibromo-1,5-naphthalenediol have so far failed, because bromine is lost under the ring-closure conditions employed.[14]

In consequence we blocked the 2- and 6-positions with alkyl groups as in **4b–g** in order to obtain **2b–g**. We used the 2,6-dipropyl-1,5-naphthalenediol (**7a**) and 2,6-dimethyl-1,5-naphthalenediol (**7b**) as starting materials for **4b–g**. Compound **7a** was obtained by a double Claisen allylic rearrangement of **8** to **9** followed by catalytic hydrogenation to yield **10**. Subsequent hydrolysis of **10** provided **7a** as shown in Scheme II.

The synthesis of **7b** is depicted in Scheme III. Compound **11** was obtained by a double Mannich reaction[15] of 1,5-naphthalenediol. We found that direct hydrogenolysis of the benzylic amine (**11**) to **7b** using palladium catalyst

Scheme II



Scheme III

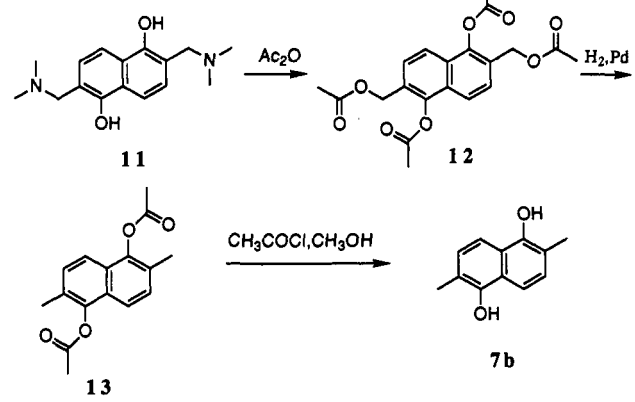


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Table I. Electrochemical Data[a]

compd	$E_{1/2}^{(1)}$, V	$E_{1/2}^{(2)}$, V	ΔE, V
2b	0.32	1.00	0.68
2c	0.22	0.82	0.60
2d	0.33	1.00	0.67
2e	0.29	0.97	0.68
2f	0.38	1.10	0.72
2g	0.25	0.86	0.6

[a] Potentials were measured at a scan rate of 100 mV/s using Pt versus SCE in 0.1 M Bu_4NPF_6/CH_2Cl_2.

failed because one ring in the naphthalene was also hydrogenated.[14] In general the direct hydrogenolysis of Mannich bases derived from phenols is difficult to control.[16] We found that the transformation of the Mannich product **11** by tetracetylation[16,17] to **12** followed by hydrogenolysis in triethylamine–ethanol gave **13** in good yield. Base-promoted hydrogenolysis is an alternative to the previously reported acid-promoted hydrogenolysis[16] of similar molecules. Compound **13** was hydrolyzed quantitatively to **7b**.

The electrochemical properties of the 1,6-dioxapyrenes, **2b–g**, were investigated by cyclic voltammetry. All the new donors undergo two reversible one-electron oxidations in dichloromethane. The halfwave potentials are given in Table I. We note that, in this series, alkyl substituents in the 2,7-positions (compounds **2c** and **2g**) lower the first oxidation potential, whereas alkyl vs aryl substituents in the 3,8-positions have a less pronounced effect. This is in agreement with a relatively large HOMO density in the 2,7-positions of the parent ring system as estimated from simple MO calculations.[14]

Compounds **2d** and **2e** were treated with 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) to give charge-transfer salts, and simple cation radical salts of **2b** were prepared by electrochemical oxidation in the presence of anions such as PF_6^-, AsF_6^-, etc. as described in the Experimental Section. These salts derived from **2b–g** are currently being investigated, and the results will be published in a forthcoming paper.

Experimental Section

Representative Procedure for Preparation of 1,6-Dioxapyrenes (2b–g). 4,9-Diphenyl-2,5,7,10-tetramethyl-1,6-dioxapyrene (2g). Compound **4g** (7.5 g, 17 mmol) was dissolved in 100 mL of CH_2Cl_2, 10 mL of CH_3SO_3H was added,[18] and the solution was stirred at rt overnight. The solution was shaken with a mixture of 250 mL of water, 125 mL of 2M NaOH, 5 g of $Na_2S_2O_4$, and 250 mL of CH_2Cl_2. The blue color of the radical ion disappeared, and the mixture became tea-colored. The organic phase was dried ($MgSO_4$), the solvent was removed, and the residue was purified by chromatography on silica gel 60 (0.063–0.200 mm) with toluene as eluent. The crude material was crystallized from toluene. Orange crystals. Yield: 2.4 g (35% from **7b**). Mp: 249–251 °C. Anal. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81. Found: C, 86.65; H, 5.88. ^1H NMR[19] (CS_2/CD_2Cl_2): δ 1.63 (s, 6 H), 1.81 (s, 6 H), 5.61 (s, 2 H), 7.15–7.34 (m, 12 H). MS: 416 (M^+), 313, 208.

2,4,7,9-Tetramethyl-1,6-dioxapyrene (2b). Yellow crystals. Yield: 28% (from **7b**). Mp: 218–220 °C. Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.88; H, 6.16. ^1H NMR[19] (CS_2/CD_2Cl_2): δ 1.59 (d, 6 H), 1.92 (s, 6 H), 6.07 (m, 4 H). MS: 264 (M^+), 249, 235, 221, 206, 189, 165, 132.

2,4,5,7,9,10-Hexamethyl-1,6-dioxapyrene (2c). Yellow crystals. Yield: 15% (from **7b**). Mp: 250–252 °C. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.65; H, 7.08. ^1H NMR[19] (CS_2/CD_2Cl_2): δ 1.67 (s, 6 H), 1.89 (s, 6 H), 1.96 (s, 6 H), 6.08 (s, 2 H).

4,9-Diethyl-2,7-dimethyl-1,6-dioxapyrene (2d). Yellow crystals. Yield 45% (from **7b**). Mp: 187–189 °C. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 82.44; H, 7.02. ^1H NMR[19] ($CDCl_3$): δ 1.16 (t, 6 H, J = 2.7 Hz), 1.98–2.25 (m, 10 H), 6.21 (m, 4 H). MS: 292 (M^+), 277, 263, 131.

4,9-Dimethyl-2,7-dipropyl-1,6-dioxapyrene (2e). Yellow crystals. Yield: 26% (from **7a**). Mp: 179–181 °C. Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.46; H, 7.55. Found: C, 82.54; H, 7.50. ^1H NMR[19] ($CDCl_3$): δ 0.92 (t, 6 H, J = 7.6 Hz), 1.54 (m, 10 H), 2.35 (t, 4 H, J = 7.6 Hz), 6.15 (m, 4 H). MS: 320 (M^+), 291, 262, 189, 145.

4,9-Diphenyl-2,7-dimethyl-1,6-dioxapyrene (2f). Orange crytals. Yield: 11% (from **7b**). Mp: 245–246 °C. Anal. Calcd for $C_{28}H_{20}O_2$: C, 86.57; H, 5.19. Found: C, 86.60; H, 5.19. ^1H NMR[19] (CS_2/CD_2Cl_2): δ 1.83 (s, 6 H), 6.04 (s, 2 H), 6.14 (s, 2 H), 7.29 (m, 10 H). MS: 388 (M^+), 359, 195, 158.

Representative Procedure for Preparation of 4b–g from 7a and 7b. 1,5-Bis(1-phenyl-1-oxo-2-ethoxy)-2,6-dimethylnaphthalene (4f). To a degassed, stirred suspension of dry K_2CO_3 (9.7 g, 0.07 mol) in 100 mL of DMF was added **7b** (5.0 g 0.03 mol) followed by 2-chloro-1-phenylethanone (8.2 g, 0.05 mol). The slurry was stirred overnight at rt. (The reaction can easily be followed by TLC on silica gel/ether–petroleum ether (1:1). The spots are visualized simply by heating.) The reaction mixture was poured into 500 mL of water. The product was filtered, washed with water, and dried. Yield: 13 g (100%) of dark brown material. Crude yields of **4b–g** were similar. This material was sufficiently pure for the next step. An analytical sample was purified by chromatography on silica gel 60 (0.063–0.200 mm) with ether–petroleum ether (1:1) as eluent followed by crystallization from EtOAc (activated carbon). Mp: 174–176 °C. Anal. Calcd for $C_{28}H_{24}O_4$: C, 79.23; H, 5.70. Found: C, 79.58; H, 5.72. ^1H NMR: ($CDCl_3$) δ 2.45 (s, 6 H), 5.27 (s, 4 H), 8.01–7.23 (m 14 H).

2,6-Dimethyl-1,5-bis(2-oxopropoxy)naphthalene (4b). An analytical sample was purified by chromatography on aluminum oxide 90 (Brockmann II-III). Eluent: ether. Mp: 156–158 °C. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.19; H, 6.87. ^1H NMR ($CDCl_3$): δ 2.36 (s, 6 H), 2.41 (s, 6 H), 4.52 (s, 4 H), 7.30 (d, 2 H, J = 8.6 Hz), 7.75 (d, 2 H, J = 8.5 Hz).

2,6-Dimethyl-1,5-bis(2-oxo-3-butoxy)naphthalene (4c). An analytical sample was purified by chromatography on silica gel 60 (0.040–0.063 mm) with ether–petroleum ether (1:1) followed by crystallization from ether. Mp: 86–90 °C. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 73.28; H, 7.46. ^1H NMR ($CDCl_3$): δ 1.36 (d, 6 H, J = 7.0 Hz), 2.41 (s, 6 H), 2.48 (s, 6 H), 4.60 (m, 2 H), 7.30 (d, 2 H, J = 8.6 Hz), 7.75 (d, 2 H, J = 8.6 Hz).

2,6-Dimethyl-1,5-bis(2-oxo-1-butoxy)naphthalene (4d). An analytical sample was crystallized from cyclohexane (activated carbon). Mp: 103–105 °C. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.60; H, 6.79. Found: C, 73.14; H, 7.35. ^1H NMR ($CDCl_3$): δ 1.89 (t, 6 H, J = 7.0 Hz), 2.41 (s, 6 H), 2.70 (q, 4 H, J = 7.3 Hz), 4.53 (s, 4 H), 7.30 (d, 2 H, J = 8.5 Hz), 7.90 (d, 2 H, J = 8.5 Hz).

2,6-Dipropyl-1,5-bis(2-oxopropoxy)naphthalene (4e). An analytical sample was crystallized from cyclohexane (activated carbon). Mp: 99–100 °C. Anal. Calcd for $C_{20}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.56; H, 8.11. ^1H NMR ($CDCl_3$): δ 1.03 (t, 6 H, J = 7.3 Hz), 1.72 (m, 4 H), 2.38 (s, 6 H), 2.68 (t, 4 H, J = 7.0 Hz), 4.53 (s, 4 H), 7.35 (d, 2 H, J = 8.9 Hz), 7.82 (d, 2 H, J = 8.9 Hz). ^{13}C NMR ($CDCl_3$): δ 14.2, 23.9, 26.6, 31.7, 118.2, 128.0, 128.5, 130.5, 151.7, 204.7.

2,6-Dimethyl-1,5-bis(1-oxo-1-phenyl-2-propoxy)naphthalene (4g). An analytical sample was crystallized from cyclohexane–toluene (10:2) (activated carbon). Mp: 135–140 °C. Anal. Calcd for $C_{30}H_{28}O_4$: C, 79.62; H, 6.24. Found: C, 79.80; H, 6.35. ^1H NMR ($CDCl_3$): δ 1.60 (d, 6 H, J = 6.7 Hz), 2.40 (s, 6 H), 5.40 (q, 2 H, J = 6.7 Hz), 7.17–8.03 (m, 14 H).

2,6-Dipropyl-1,5-naphthalenediol (7a). The hydrolysis was performed as described for **7b**. Yield: 100%. An analytical sample was purified by sublimation (150 °C, 0.1 mbar). White crystals. Mp: 167–169 °C. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.51; H, 8.40. ^1H NMR ($CDCl_3$): δ 1.04 (t, 6 H, J

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(19) NMR spectra of **2b–g** were recorded with 1 drop of 2 M $Na_2S_2O_4$ in the tubes to prevent line broadening due to (air) oxidation to the corresponding cation radicals.

= 7.0 Hz), 1.73 (m, 4 H), 2.76 (t, 4 H, J = 7.9 Hz), 7.26 (d, 2 H, J = 8.5 Hz), 7.59 (d, 2 H, J = 8.5 Hz).

2,6-Dimethylnaphthalene-1,5-diol (7b). Acetyl chloride (10 mL) was added to a mixture of **13** (12.9 g, 0.05 mol) and 125 mL of methanol. After refluxing overnight, the solution was evaporated to dryness. This material can be used directly without purification. Yield: 8.6 g (91%). An analytical sample sublimated at 150 °C/0.1 mbar had mp 208–210 °C. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.68; H, 6.58. ^{1}H NMR (DMSO-d_6): δ 2.32 (s, 6 H), 7.15 (d, 2 H, J = 8.6 Hz), 7.63 (d, 2 H, J = 8.6 Hz), 8.77 (s, 2 H). ^{13}C NMR (DMSO-d_6): δ 16.19, 112.89, 116.86, 125.18, 128.05, 149.38.

1,5-Di-2-propenoxynaphthalene (8). To a degassed suspension of dry, powdered K_2CO_3 (58.0 g, 0.41 mol) in 200 mL of DMF was added 1,5-naphthalenediol (32.0 g, 0.20 mol) followed by 3-bromopropene (50.8 g, 0.42 mol). After being stirred overnight, the mixture was poured into water (600 mL). The material was filtered and dried in vacuo. The dark material can be purified by passage through a short column of silica gel with CH_2Cl_2 as eluent. Yield: 37.0 g (77%). ^{1}H NMR ($CDCl_3$): δ 5.15–5.58 (m, 4 H), 5.89–6.35 (m, 2 H), 6.70 (d, 2 H, J = 7.6 Hz), 7.28 (m, 2 H), 7.85 (d, 2 H, J = 8.5 Hz).

2,6-Di-2-propenyl-1,5-naphthalenediol Diacetate (9). A mixture of crude **8** (≤0.20 mol), 125 mL of *N,N*-diethylaniline, and 125 mL of acetic anhydride was refluxed 24 h,[20] allowed to cool, and stirred into a solution of 125 mL of concd HCl in 1 L of water. The solid was filtered, washed with water, dissolved in boiling absolute ethanol (750 mL), treated with activated carbon, filtered, and cooled (5 °C). The product was filtered and dried in vacuo. Yield: 34.8 g (54% from 1,5-naphthalenediol). Mp: 141–143 °C. Anal. Calcd for $C_{20}H_{20}O_4$: C, 74.06; H, 6.21. Found: C, 74.28; H, 6.30. ^{1}H NMR ($CDCl_3$): δ 2.45 (s, 6 H), 3.53 (d, 4 H, J = 6.4 Hz), 4.97–5.28 (m, 4 H), 5.57–6.21 (m, 2 H), 7.34 (d, 2 H, J = 8.9 Hz), 7.57 (d, 2 H, J = 8.5 Hz).

2,6-Dipropyl-1,5-naphthalenediol Diacetate (10). **9** (10.0 g, 0.03 mol), 0.5 g of 10% Pd/C, and 250 mL of absolute ethanol were hydrogenated in a standard low-pressure apparatus. When the hydrogen uptake ceased, the suspension was heated to near reflux and filtered through a bed of Celite. The filtrate was cooled (-20 °C), and the product was filtered and dried. Yield: 75%. Mp: 125–127 °C. Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.66; H, 7.31. ^{1}H NMR ($CDCl_3$): δ 0.96 (t, 6 H, J = 7.9 Hz), 1.65 (m, 4 H), 2.41 (s, 6 H), 2.62 (t, 4 H, J = 8.0 Hz), 7.38 (d, 2 H, J = 8.5 Hz), 7.61 (d, 2 H, J = 8.5 Hz).

2,6-Bis[(*N,N*-dimethylamino)methyl]-1,5-naphthalenediol (11).[15] Powdered naphthalene-1,5-diol (52.0 g, 0.19 mol) was added to a stirred and cooled (10 °C) mixture of 100 mL of 24.5% aqueous formaldehyde and 200 mL of 40% aqueous $(CH_3)_2NH$ in 1 L of absolute ethanol. After 20 min the cooling bath was removed, and stirring was continued at rt for 45 min. The product was filtered, washed with a little absolute ethanol, and dried in vacuo. White crystal. Yield: 75.0 g (84%). Mp: 170 °C dec (lit.[15] mp 176 °C). Anal. Calcd for $C_{16}H_{22}N_2O_2$: C, 70.04; H, 8.08; N, 10.21. Found: C, 70.48; H, 8.20; N, 10.14. ^{1}H NMR ($CDCl_3$): δ 2.37 (s, 12 H), 3.77 (s, 4 H), 7.02 (d, 2 H, J = 8.5 Hz), 7.66 (d, 2 H, J = 8.2 Hz), 10.59 (s, 2 H).

2,6-Bis(hydroxymethyl)-1,5-naphthalenediol Tetraacetate (12). Phenol **11** (80.0 g, 0.29 mol) was added in small portions under vigorous stirring to 400 mL of acetic anhydride. The reddish solution was refluxed for 8 h. Excess acetic anhydride was hydrolyzed, while the mixture was hot, by very cautious addition of water (100 mL). (**CAUTION: violent reaction!**) The hot solution was poured into 1.6 L of water with stirring. The precipitated product was filtered, washed with water, and dried in vacuo at 80 °C. Off-white crystals. Yield: 105 g (93%). Mp: 158–161 °C. Anal. Calcd for $C_{20}H_{20}O_8$: C, 61.85; H, 5.19. Found: C, 61.51; H, 4.94. ^{1}H NMR ($CDCl_3$): δ 2.08 (s, 6 H), 2.48 (s, 6 H), 5.20 (s, 4 H), 7.56 (d, 2 H, J = 8.6 Hz), 7.71 (d, 2 H, J = 8.5 Hz).

2,6-Dimethyl-1,5-naphthalenediol Diacetate (13). A mixture of **12** (30.0 g, 0.08 mol), 1 g of 10% Pd on activated carbon, 600 mL of absolute ethanol, and 30 mL of Et_3N was hydrogenated in a standard low-pressure hydrogenation apparatus at 65–70 °C. The catalyst was removed from the hot reaction mixture by filtration through a bed of Celite. The product separated upon cooling of the filtrate. White crystals. Yield: 15.8 g (75%). Mp: 187–189 °C. Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.55; H, 5.77. ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 6 H), 2.40 (s, 6 H), 7.30 (d, 2 H, J = 8.6 Hz), 7.56 (d, 2 H, J = 8.6 Hz). ^{13}C NMR ($CDCl_3$): δ 16.26, 20.48, 118.68, 126.16, 126.94, 129.35, 144.43, 168.69.

2d–TCNQ (1:1). **2d** (60 mg, 2 mmol) was dissolved in a minimal amount of hot benzonitrile and mixed with a solution of TCNQ (40 mg, 2 mmol) in acetonitrile. The mixture was allowed to cool slowly, and a black crystalline solid separated in ca. 70% yield. Anal. Calcd for $C_{32}H_{24}H_4O_2$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.98; H, 4.85; N, 11.54.

2g–TCNQ (1:1). This material was described as for **2d**–TCNQ from acetonitrile–toluene. Yield: 52%. Anal. Calcd for $C_{42}H_{28}N_4O_2$: C, 81.27; H, 4.55; N, 9.03. Found: C, 81.60; H, 4.55; N, 9.10.

(2b)$_2$PF$_6$. 50 mL of a 0.02 M solution of **2b** in 1,1,2-trichloroethane containing *n*-Bu_4PF_6 (0.1 M) was electrolyzed at constant current (2 μamp) using a platinum wire (20 mm, diameter 0.5 mm) as the working electrode, in a standard two-compartment cell. After ca. 60% conversion, the black needlelike crystals were harvested and washed with a little pure solvent. Yields vary from 40 to 60% based on the amount of current passed. Anal. Calcd for $C_{36}H_{20}O_4PF_6$: C, 64.19; H, 4.79. Found: C, 64.19; H, 4.84.

(2b)$_2$AsF$_6$. This material was prepared as described for **(2b)$_2$PF$_6$**. Anal. Calcd for $C_{36}H_{20}O_4AsF_6$: C, 60.26; H, 4.49. Found: C, 60.22; H, 4.60.

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