Tetrafluoro and dichloro derivatives of thiophene-fused DCNQI- and TCNQ-type acceptors: a synthetic, electrochemical and crystallographic study

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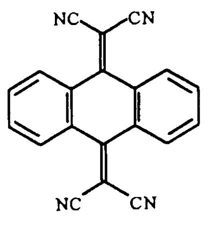
Novel thiophene-fused DCNQI derivatives **8** and **11** bearing four fluorine atoms have been obtained in good yield from the corresponding quinones by reaction with bis(trimethylsilyl)carbodiimide (BTC). The presence of four fluorine atoms leads to good acceptor molecules which form charge transfer complexes in solution with *N,N′*-tetramethyl-*p*-phenylenediamine. The effect of chlorine atoms on the crystal packing in the analoguous thiophene-fused TCNQ derivatives **3a** and **3b** is also reported.

Tetracyano-*p*-quinodimethane (TCNQ) and dicyano-*p*-quinodiimine (DCNQI) have been used most widely as acceptors[1] for the preparation of novel charge transfer complexes (CTC) and charge transfer salts.[2]

On the other hand, the electron acceptors containing benzene-fused TCNQ and DCNQI derivatives **1** and **2**, prepared from 9,10-anthraquinone,[3,4] do not form CTC when they are mixed with donor molecules such as tetrathiafulvalene (TTF). This is due to their poor acceptor ability and, particularly, the highly distorted structure of **1**. Although the same result was found for the acceptors **3** and **4** obtained from 4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione, the condensation of a thiophene ring instead of a benzene ring resulted in a more planar molecule.[5]



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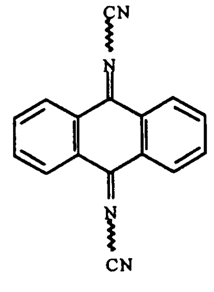

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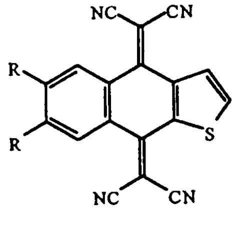
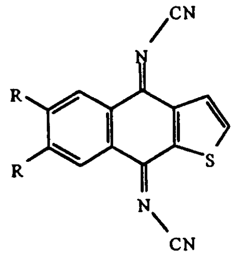


3a R = H
b R = Cl



4a R = H
b R = Cl

Taking into account the strong effect of fluorine or chlorine atoms on the acceptor capacity,[6] we have carried out the synthesis of novel DCNQI acceptors **8** and **11** derived from 9,10-anthraquinone and 4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione bearing four fluorine atoms on the benzene ring. The geometry of these DCNQI-type acceptors may present greater planarity than the corresponding TCNQ-type analogues, due to the less sterically demanding cyanoimino group in comparison with the dicyanomethylene fragment. In a previous paper[5b] we carried out a comparative crystallographic study of compounds of this type and important differences in terms of planarity and crystal packing were found due to the highly distorted geometry in **3a**. Considering the effect that substituents can play on the stacking pattern, we have determined the X-ray structure of compound **3b** bearing two chlorine atoms.

Results and Discussion

The synthesis of the novel π-extended DCNQI-type derivatives **8** and **11** was carried out from the corresponding halogeno-substituted quinones **7** and **10** by reaction with bis(trimethylsilyl)carbodiimide (BTC) by following Hünig's procedure (Scheme 1).[7] The quinones **7** and **10** were prepared from tetrafluorophthalic anhydride **5** by reaction with benzene and aluminium trichloride to yield the corresponding 2-benzoyl-3,4,5,6-tetrafluorobenzoic acid **6** which, by treatment with concentrated sulfuric acid at 100 °C, led to the 1,2,3,4-tetrafluoroanthraquinone **7**. In a similar way, the reaction of anhydride **5** with thienyllithium in diethyl ether at −78 °C yielded the acid **9** which, after treatment with PCl_5 and $AlCl_3$ in dry nitrobenzene gave the novel 5,6,7,8-tetrafluoro-4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione **10** (see Experimental section). An alternative procedure for the preparation of substituted naphtho[2,3-*b*]thiophenediones by microwave assisted cyclization of substituted 2-thienylcarbonylbenzoic acids, catalysed with clays in dry media, has been recently described.[8]

Compounds **8** and **11** can exist as the *syn* and *anti* isomers. The presence of isomers in other DCNQI analogues has been previously established by NMR spectroscopy[4] and molecular mechanics analyses.[9] The high resolution ^1H NMR spectrum of compound **8** shows a sharp doublet of doublets at δ 7.93 and a broad signal at δ 8.67 due to the rapid isomerization of the cyanoimino group at room temperature. This fact could be accounted for by the similar steric hindrance of hydrogen and fluorine *peri* atoms, resulting in a non-favoured configuration.[4,9] Accordingly, compound **11** showed a sharp doublet at δ 8.09 and another at δ 8.80 suggesting a favoured configuration with the cyano groups towards the thiophene ring, in agreement with the previously reported X-ray data for the unsubstituted compound **4a**.[5b]

Cyclic voltammetric (CV) measurements of compounds **8** and **11**, as well as the starting quinones **7** and **10**, were carried out in CH_2Cl_2 at room temperature using tetrabutylammonium perchlorate as the supporting electrolyte. The data obtained are summarized in the Table 1. All compounds showed two

Table 1 Cyclic voltammetry data of acceptors

compound	$E_{1/2}{}^1$/V	$E_{1/2}{}^2$/V	ΔE	log K
1[a]	-0.20 ($2e^-$)			
2[a]	-0.11	-0.46	0.35	5.93
3a[a]	-0.18 ($2e^-$)			
3b[b]	-0.10 ($2e^-$)			
4a[b]	-0.11	-0.61	0.50	8.62
4b[b]	-0.04	-0.50	0.46	7.93
7[c]	-0.72	-1.23	0.51	8.79
8[c]	-0.19 (-0.19)[b]	-0.50 (-0.48)[b]	0.31	5.34
10[c]	-0.57	-1.08	0.51	8.79
11[c]	0.00	-0.46	0.46	7.93
DCNQI[c]	0.21	-0.41	0.62	10.68

[a] $CH_2Cl_2/Bu_4N^+BF_4^-/Pt$ *vs.* Ag/AgCl/MeCN (refs. 4, 5). [b] $MeCN/Bu_4N^+ClO_4^-$/glassy carbon *vs.* Ag/Ag^+ (ref. 6). [c] $CH_2Cl_2/Bu_4N^+BF_4^-$/glassy carbon *vs.* SCE; scan rate 50 mV s^{-1}.

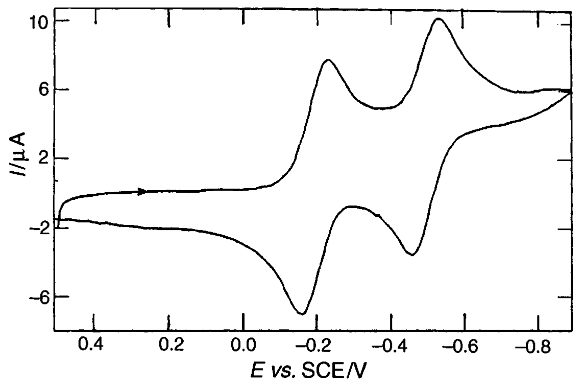
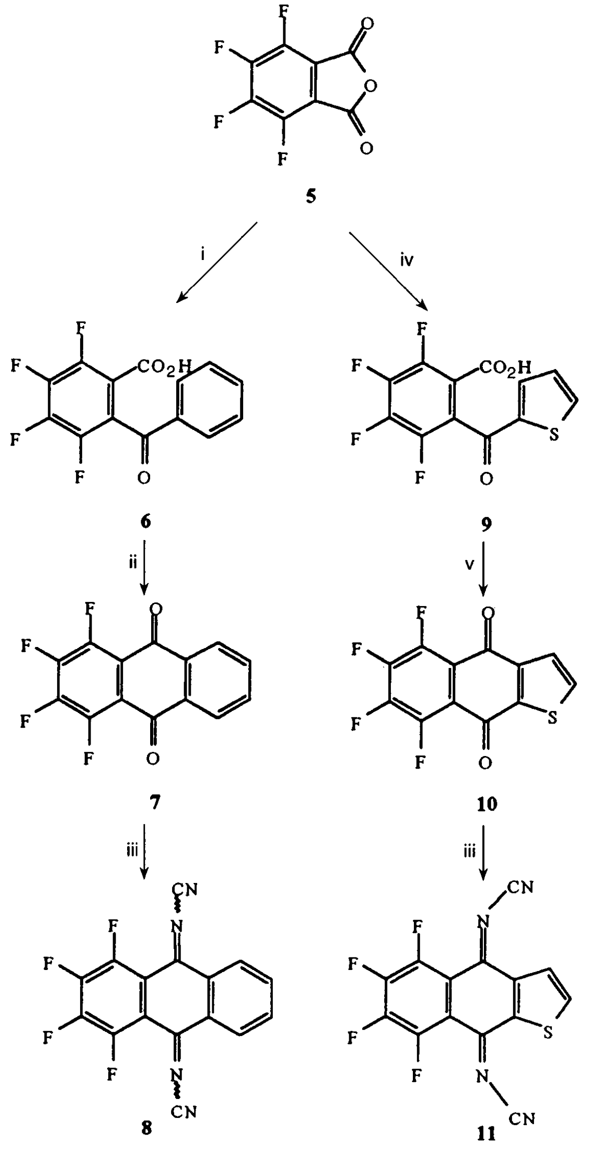


Fig. 1 Cyclic voltammetry of compound **8** (scan rate 50 mV s^{-1})

one-electron reduction waves to the corresponding anion-radical and dianion (Fig. 1). Replacing the benzene ring with a thiophene ring leads to a better acceptor due to the lowering of the steric hindrance. The presence of four fluorine atoms as substituents on the benzene ring significantly decreases the reduction potential values. The reduction potential values found for compounds **8** and **11** clearly confirm these trends, and the thiophene-containing compound **11** exhibits a first reduction potential which is shifted 190 mV to more positive values (Table 1).



Scheme 1 Reagents and conditions: i, C_6H_6, $AlCl_3$; ii, H_2SO_4; iii, $Me_3SiN{=}C{=}NSiMe_3$, $TiCl_4$, CH_2Cl_2; iv, 2-thienyllithium, then NH_4Cl, HCl; v, PCl_5, $C_6H_5NO_2$, $AlCl_3$

Increasing benzannulation with regard to the parent DCNQI leads to a decrease in the acceptor ability and also to a diminishing of the thermodynamic stability of the corresponding radical-anions (lower log K values[10] in Table 1). Thus, compound **8** exhibits the least stable radical-anion due to the stronger steric interaction between the cyano group and the *peri*-hydrogens.

Unlike the non-fluorine substituted analogues, compounds **8** and **11** show evidence of complexation when they were mixed, in equimolecular amounts in dichloromethane under inert atmosphere, with the strong donor *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPD). Although solid stable CTCs were not isolated, a colour change was observed. The UV–VIS spectra of the reaction solution, under argon atmosphere, showed a typical low-energy charge-transfer band (**8**·TMPD: $\lambda_{max} = 538$ nm; **11**·TMPD: $\lambda_{max} = 545$ nm). Attempts to form CT-complexes with acceptor **11**, which showed the best acceptor ability in this study, with other donors such as tetrathiafulvalene (TTF) did not afford the corresponding solid CT-complex. A weak broad band was observed at around 450 nm in the electronic spectrum which might indicate the presence of a very low energy CT-band in solution. These findings are also in agreement with those previously reported for the poorer electron-acceptor dithiophene-fused TCNQ {4,8-bis(dicyanomethylene)-4,8-dihydrobenzo-[1,2-*c*:4,5-*c*′]dithiophene}[11] which, in contrast to the other isomers, did not form a CT-complex with TTF. Finally, attempts to form a metal salt were carried out by reaction of acceptors **8** and **11** with copper iodide in acetonitrile under inert atmosphere. A black solid precipitate was only obtained with **8**, which showed the IR stretching cyano band at 2177 cm^{-1}. According to the elemental analysis, a rather unusual 1 : 5 acceptor–copper stoichiometry was found.

The molecular structures of compounds **3b** and the unsubstituted analogue **3a** are shown in Fig. 2, together with the atomic numbering scheme. The main geometrical features of the common moiety of both compounds are quite similar, and only bond distances and angles involving atoms of the thiophene ring show significant differences (Table 2). This effect could be due to an artifact of the disorder which both molecules possess. Thus, the presence of the two chlorine atoms in compound **3b** does not affect significantly the conformation of this molecule. Both compounds present a butterfly shape centred at the two substituted carbon atoms, with an interplanar angle between the S(1)–C(2)–C(3)–C(4)–C(5)–C(12)–C(13) and C(5)–C(6)–C(7)–C(8)–C(9)–C(10)–C(11)–C(12) planes of 147.5° (1) for compound **3b** and 149.7° (1) for compound **3a**. This distortion from planarity has been accounted for by the steric hindrance between the cyano

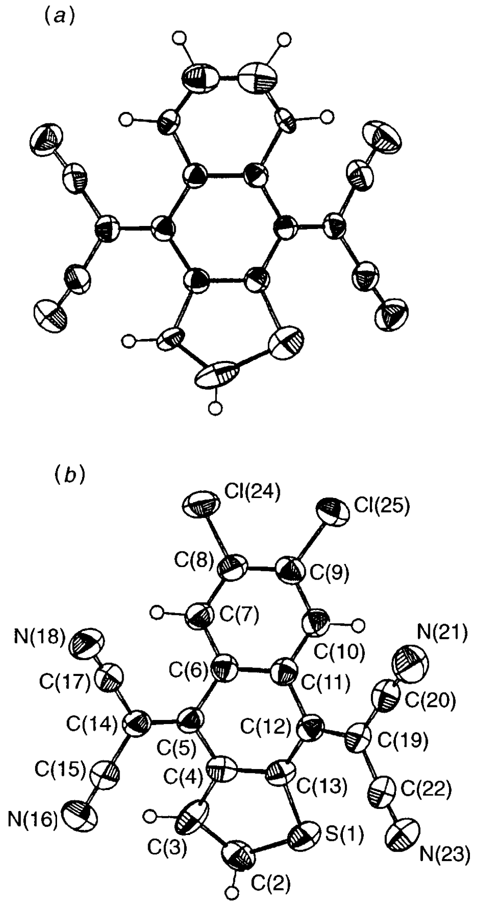


Fig. 2 Molecular structure of compounds (*a*) **3a** and (*b*) **3b**, showing the atomic numbering

groups and the *peri* hydrogens. This butterfly shape of the molecules **3a** and **3b** with a boat type quinonoid group was also found in 11,11,12,12-tetracyano-9,10-anthraquinodimethane (TCAQ).[12] Different isomeric benzodithiophene analogues of TCAQ have also been obtained and their electronic and steric properties were found to depend on the mode of fusion of the two thiophene units to the central TCNQ ring.[11] The crystal structures of these thiophene-fused TCNQs showed a more planar butterfly shape, in comparison with the TCAQ molecule.

On the other hand, crystal packing is severely modified (Fig. 3). Compound **3b** shows aromatic interactions, forming dimers and Cl···N[13] contacts in the crystal packing, and with a contact Cl(25)···Cl(24) ($x-1/2$, y, $1/2-z$) of 3.461 (2) Å. However, compound **3a** presents the aromatic interactions as the main intermolecular contacts, forming a stacking pattern along the (2 0 1) direction with tight packing. Thus it seems that, here again, the chlorine atoms, when competing with the rings interactions, play a role in the packing.

Both molecules **3a** and **3b** present structural disorder, consisting of the superposition of two ordered structures related by a pseudo mirror plane through C(2) and the mid-point of C(8)–C(9). The population factors were 0.53–0.47(1) and 0.72–0.298(1) for both compounds **3b** and **3a**, respectively, thus showing the symmetrizing effect of the chlorine atoms. The disorder was constrained in the refinement so as to fit the pseudo mirror plane with the populations equal to 1.

In conclusion, we have carried out the synthesis, electrochemical and crystallographical study of some novel halogen-containing acceptors. The presence of four fluorine atoms is responsible for the greater acceptor ability of **8** and **11** as shown by the cyclic voltammetry study. The reasonably good first reduction potentials, in addition to the expected planar

Table 2 Geometrical features of compounds **3**[a]

bond lengths/Å	**3b**	**3a**
S(1)–C(2)	1.80(1)	1.68(2)
S(1)–C(13)	1.648(3)	1.66(2)
C(2)–C(3)	1.37(1)	1.30(6)
C(3)–C(4)	1.541(5)	1.46(6)
C(4)–C(5)	1.462(4)	1.458(4)
C(4)–C(13)	1.393(6)	1.391(5)
C(5)–C(6)	1.465(5)	1.471(5)
C(5)–C(14)	1.36(1)	1.373(5)
C(6)–C(7)	1.469(5)	1.383(5)
C(6)–C(11)	1.405(6)	1.415(4)
C(7)–C(8)	1.29(1)	1.399(6)
C(8)–C(9)	1.31(1)	1.388(5)
C(8)–Cl(24)	—	1.713(4)
C(9)–C(10)	1.265(6)	1.380(5)
C(9)–Cl(25)	—	1.719(4)
C(10)–C(11)	1.484(5)	1.392(5)
C(11)–C(12)	1.469(4)	1.468(5)
C(12)–C(13)	1.453(4)	1.454(5)
C(12)–C(19)	1.363(5)	1.362(5)
C(14)–C(15)	1.432(7)	1.425(6)
C(14)–C(17)	1.430(5)	1.435(5)
C(15)–N(16)	1.142(7)	1.150(6)
C(17)–N(18)	1.152(5)	1.141(6)
C(19)–C(20)	1.436(5)	1.441(5)
C(19)–C(22)	1.440(5)	1.433(6)
C(20)–N(21)	1.140(5)	1.133(6)
C(22)–N(23)	1.144(6)	1.139(6)
bond angles/degrees		
C(2)–S(1)–C(13)	93.1(3)	94(1)
S(1)–C(2)–C(3)	114.1(5)	113(3)
C(2)–C(3)–C(4)	105.4(5)	110(4)
C(3)–C(4)–C(13)	115.4(4)	112(3)
C(3)–C(4)–C(5)	124.9(4)	128(3)
C(5)–C(4)–C(13)	119.7(3)	120.3(3)
C(4)–C(5)–C(14)	122.4(3)	122.3(3)
C(4)–C(5)–C(6)	114.6(3)	114.4(3)
C(6)–C(5)–C(14)	122.8(3)	123.3(3)
C(5)–C(6)–C(11)	119.0(3)	118.8(3)
C(5)–C(6)–C(7)	125.3(4)	122.2(3)
C(7)–C(6)–C(11)	115.7(3)	119.0(3)
C(6)–C(7)–C(8)	121.7(4)	120.8(3)
C(7)–C(8)–C(9)	122.6(5)	119.4(4)
C(7)–C(8)–Cl(24)	—	117.0(3)
C(9)–C(8)–Cl(24)	—	123.6(3)
C(8)–C(9)–C(10)	122.3(5)	120.7(4)
C(8)–C(9)–Cl(25)	—	120.5(3)
C(10)–C(9)–Cl(25)	—	118.8(3)
C(9)–C(10)–C(11)	122.2(4)	120.0(4)
C(6)–C(11)–C(10)	115.4(3)	119.9(4)
C(10)–C(11)–C(12)	124.9(3)	121.1(3)
C(6)–C(11)–C(12)	119.7(3)	118.9(3)
C(11)–C(12)–C(19)	122.4(3)	122.9(3)
C(11)–C(12)–C(13)	114.4(3)	113.9(3)
C(13)–C(12)–C(19)	123.2(3)	122.9(3)
C(4)–C(13)–C(12)	120.0(3)	119.1(3)
S(1)–C(13)–C(12)	128.2(3)	130.9(4)
S(1)–C(13)–C(4)	111.8(3)	109.9(4)
C(5)–C(14)–C(17)	124.0(4)	124.2(4)
C(5)–C(14)–C(15)	124.0(4)	123.3(4)
C(15)–C(14)–C(17)	111.6(4)	112.4(4)
C(14)–C(15)–N(16)	174.1(5)	175.8(4)
C(14)–C(17)–N(18)	175.9(5)	176.2(5)
C(12)–C(19)–C(22)	123.5(4)	122.3(3)
C(12)–C(19)–C(20)	124.8(4)	123.2(4)
C(20)–C(19)–C(22)	111.7(4)	114.0(3)
C(19)–C(20)–N(21)	175.4(5)	175.9(5)
C(19)–C(22)–N(23)	177.2(5)	178.5(5)

[a] Both compounds present disorder. Distances and angles are given for the major structure.

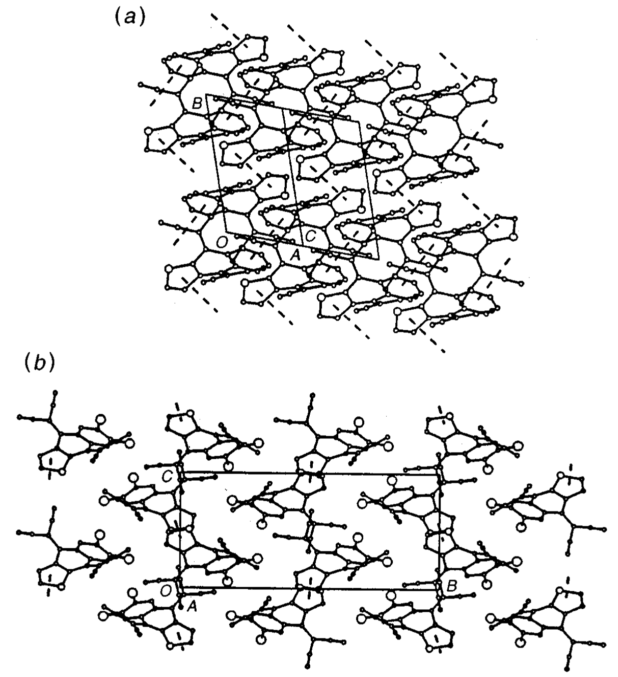


Fig. 3 Crystal packing for (*a*) compound **3a** along the axis perpendicular to the (2 0 1) direction and (*b*) compound **3b** along the *a* axis. Aromatic interactions are represented with dashed lines.

geometry for compounds **8** and **11**, are responsible for the complexation observed in the UV–VIS spectra when they are in solution in the presence of *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine. Although these novel acceptors did not form CT-complexes with TTF, a copper CT-salt was formed with compound **8**. On the other hand, the presence of halogen atoms also plays an important role in the crystal packing, as observed in the intermolecular interactions of the related compounds **3a** and **3b**. These data indicate that although the presence of fluorine atoms increases the acceptor ability in these aryl-fused DCNQI derivatives, they are not strong enough acceptors to form CT-complexes with molecules which form stable radical-cation such as TTF. The presence of halogen atoms on molecules containing two five-membered heterocyclic rings fused to the central TCNQ and DCNQI acceptors should lead to stronger acceptors with more planar geometries.

Experimental

General

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 398 spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda-3 instrument. ^{1}H NMR spectra were determined with a Varian XL-300S spectrometer and *J* values are given in Hz. Elemental analyses were performed on a Perkin-Elmer CHN 2400 apparatus.

Cyclovoltammetric measurements were performed on a EG & PAR Versastat potentiostat using 250 electrochemical analysis software. A Metrohm 6.084.C10 glassy carbon electrode was used as indicator electrode in voltammetric studies.

Tetrafluorophthalic anhydride, 2-thienyllithium, titanium tetrachloride and bis(trimethylsilyl)carbodiimide (BTC) are commercially available.

X-Ray crystallographic measurements

Crystal data for compound 3b. $C_{18}H_4N_4S_1Cl_2$, MW = 379.222, monoclinic, $P2_1/c$, $a = 9.229$ (1), $b = 19.609$ (4), $c = 9.457$ (1) Å, $\beta = 109.29°$, $V = 1615.4$ (4) Å, $Z = 4$, $D_C = 1.56$ g cm^{-3}, $F(000) = 760$, $\mu = 49.44$ cm^{-1}. Refined cell parameters were obtained from setting angles of 72 reflections. A prismatic brown crystal (0.30 × 0.25 × 0.15 mm) was used for the analysis.

Data collection. Automatic four circle diffractometer Philips PW 1100 with graphite oriented monochromated Cu-Kα radiation. The intensity data were collected using the ω–2θ scan mode with $2 < \theta < 65°$; two standard reflections were measured every 90 min with no intensity variation. A total of 2743 reflections were measured and 2286 were considered as observed $[I > 3\sigma(I)]$. The data were corrected for Lorentz and polarization effects.

Structure solution and refinement. The structure was solved by direct methods using SIR88[14] and DIRDIF.[15] Hydrogen atoms were calculated and fixed in the final mixed refinement; isotropic thermal parameters of these atoms were considered as fixed contributors. A convenient weighting scheme was applied[16] to obtain no dependence in $\langle w\Delta[14]F\rangle vs.\langle F_0\rangle$ and $\langle \sin\theta/\lambda\rangle$. The final *R* (*Rw*) value was 5.9 (7.4). Atomic scattering factors for the compound were taken from International Tables for X-Ray Crystallography[17] and calculations were performed using XRAY80,[18] XTAL,[19] HSEARC[20] and PARST.[21]

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/15.

2-Benzoyl-3,4,5,6-tetrafluorobenzoic acid 6

This compound was obtained from tetrafluorophthalic anhydride, benzene and $AlCl_3$ by following the standard Friedel–Crafts procedure.[22] Yield 70%; mp 177 °C (from water) (Calc. for $C_{14}H_6F_4O_3$: C, 56.39; H, 2.03. Found: C, 56.42; H, 2.12%); δ_H(300 MHz, [$^2H_6$]DMSO) 7.41–7.89 (5H, m, ArH), 14.20 (1H, br s, CO_2H); ν_{max}(KBr)/cm^{-1} 3000, 1715 (C=O, acid), 1680 (C=O), 1630, 1600, 1590, 1530, 1470, 1440, 1370, 1320.

2-(2-Thienylcarbonyl)-3,4,5,6-tetrafluorobenzoic acid 9

2-Thienyllithium (4.6 ml; 1.0 M in tetrahydrofuran) was slowly added to a mixture of tetrafluorophthalic anhydride (1 g, 4.54 mmol) in dry diethyl ether (15 ml) at −20 °C. The mixture was maintained under argon and allowed to warm to room temperature, then stirred for 24 h. The cold reaction mixture containing the lithium complex was decomposed by the addition of saturated NH_4Cl (30 ml) and then acidified with 6 M HCl. The organic layer was separated and the aqueous phase washed with diethyl ether; the organic extracts were washed with saturated brine and water, and treated with 5% sodium hydrogen carbonate (3 × 50 ml). The aqueous alkaline layers were collected, cooled and acidified by the dropwise addition of 6 M HCl with vigorous stirring. The keto acid which precipitated was filtered and washed free of the mineral acid with water. The crude product was crystallized from boiling water. Yield 60%; mp 175 °C (Calc. for $C_{12}H_4F_4O_3S$: C, 47.38; H, 1.33. Found C, 47.60; H 1.35%); δ_H(300 MHz, $CDCl_3$) 7.14 (1H, dd, *J* 3.9 and 4.8, H-4-thiophene), 7.43 (1H, d, *J* 3.9, H-5-thiophene), 7.80 (1H, dd, *J* 4.8 and 1.2 H-3-thiophene); ν_{max}(KBr)/cm^{-1} 3200, 1750 (C=O, acid), 1640 (C=O), 1520, 1480, 1420, 1370, 1300.

1,2,3,4-Tetrafluoroanthraquinone 7

Compound **7** was obtained by treatment of **6** (1 g, 3.3 mmol) with conc. sulfuric acid (5 ml) at 100 °C. The reaction mixture was cooled and poured into ice–water, and the product was collected by filtration to yield an orange solid. Yield 85%; mp 224 °C (Calc. for $C_{14}H_4F_4O_2$: C, 60.02; H, 1.44. Found: C, 60.31; H, 1.21%); δ_H(300 MHz, $CDCl_3$) 7.80 (2H, dd, *J* 5.6 and 3.3, ArH), 8.31 (2H, dd, *J* 5.6 and 3.3, ArH); ν_{max}(KBr)/cm^{-1} 3450, 1680 (C=O), 1620, 1510, 1470, 1400, 1370.

5,6,7,8-Tetrafluoro-4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-dione 10

This compound was obtained according to the reported procedure.[23] To a solution of **6** (0.5 g, 1.64 mmol) and PCl_5 (0.512 g, 2.46 mmol) in 20 ml of dry nitrobenzene, $AlCl_3$ (0.33 g, 2.46 mmol) was added. The mixture was kept at room temperature for 1 h, and then at 140 °C for 4 h. The solvent was distilled under vacuum and a black oil was obtained. The crude compound was purified by column chromatography over silica gel using hexane–ethyl acetate (4 : 1) as eluent. Further purification was accomplished by recrystallization from ethanol. Yield 55%, mp 190 °C (Calc. for $C_{12}H_2F_4O_2S$: C, 50.36; H, 0.70. Found: C, 50.14; H, 0.77%); δ_H(300 MHz, $CDCl_3$) 7.69 (1H, d, *J* 5.1, thiophene), 7.79 (1H, d, *J* 5.1, thiophene); ν_{max}(KBr)/cm^{-1} 1680 (C=O), 1630, 1540, 1510, 1480, 1410, 1380.

Condensation reaction of quinones 7 and 10 with BTC

General procedure. To a solution of the corresponding quinone (2 mmol) in dry CH_2Cl_2 (50 ml) at room temperature and under argon atmosphere, $TiCl_4$ followed by BTC were added dropwise with a syringe by using a variable stoichiometric ratio (see below). The reaction was stirred for the required time and monitored by thin layer chromatography (TLC) until the starting quinone had been consumed, when CH_2Cl_2 (200 ml) was added and the reaction mixture was poured into ice–water (200 g). The reaction was vigorously stirred until the solution reached room temperature. The organic phase was separated and washed with water (3 × 50 ml), dried ($MgSO_4$) and concentrated to 10 ml. The same volume of hexane (10 ml) was added and the solid precipitated. It was collected by filtration and washed with hexane.

***N*,*N*′-Dicyano-1,2,3,4-tetrafluoroanthraquinone diimine 8.** Compound **8** was obtained, by stirring for 24 h at room temperature and refluxing for 3 h using **7** (2.1 mmol), $TiCl_4$ (8.7 mmol) and BTC (7.4 mmol), in 60% yield; mp 149 °C (Calc. for $C_{16}H_4F_4N_4$: C, 58.55; H, 1.23. Found: C, 58.34; H, 1.37%); δ_H(300 MHz, $CDCl_3$) 7.93 (2H, dd, *J* 5.5 and 3.1, ArH), 8.67 (2H, br s, ArH); ν_{max}(KBr)/cm^{-1} 2190 (CN), 1580, 1510, 1480, 1410, 1390.

***N*,*N*′-Dicyano-5,6,7,8-tetrafluoro-4,9-dihydronaphtho[2,3-*b*]thiophene-4,9-diimine 11.** Compound **11** was obtained, by stirring for 24 h at room temperature using **10** (0.17 mmol), $TiCl_4$ (1.05 mmol) and BTC (1.19 mmol), in 90% yield; mp 194 °C (Calc. for $C_{14}H_4F_4N_4S$: C, 50.31; H, 0.60. Found: C, 50.14; H, 0.77%); δ_H(300 MHz, $CDCl_3$) 8.09 (1H, d, *J* 5.2, thiophene), 8.80 (1H, d, *J* 5.2, thiophene); ν_{max}(KBr)/cm^{-1} 2190 (CN), 1580, 1510, 1400, 1300, 1270.

Copper salt of compound 8

A boiling solution of *N*,*N*′-dicyano-1,2,3,4-tetrafluoroanthraquinone diimine **8** (200 mg, 0.6 mmol) in 20 ml of dry acetonitrile was transferred *via* cannula under argon atmosphere to a boiling solution of CuI (77 mg, 0.4 mmol) in 10 ml of dry acetonitrile; upon cooling, the resulting precipitate was filtered, washed and dried, giving the solid product in 30% yield (Calc. for $C_{16}H_4F_4N_4Cu_5$: C, 29.87; H, 0.63. Found: C, 30.67; H, 1.04%); ν_{max}(KBr)/cm^{-1} 2177 (CN), 1568, 1505, 1389, 1266.

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